ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND FUNCTIONALIZATION OF 3-ARM STAR POLYPENTAFLUOROSTYRENE VIA THIOL/PARA FLUORO CLICK REACTION

M.Sc. THESIS

Gizem PALAK

Department of Chemistry

Chemistry Programme

MAY 2014

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS AND FUNCTIONALIZATION OF 3-ARM STAR POLYPENTAFLUOROSTYRENE VIA THIOL/PARA FLUORO CLICK REACTION

M.Sc. THESIS

Gizem PALAK
(509121065)

Department of Chemistry

Chemistry Programme

Thesis Advisor: Prof. Dr. Gürkan HIZAL

MAY 2014

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÜÇ KOLLU POLİPENTAFLUROSTİREN YILDIZ POLİMERLERİN SENTEZİ VE THİOL/PARA FLORO 'CLİCK' REAKSİYONLARI İLE MODİFİKASYONU

YÜKSEK LİSANS TEZİ

Gizem PALAK
(509121065)

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Prof. Dr. Gürkan HIZAL

MAYIS 2014

Name-surname, a **M.Sc./a Ph.D.** student of ITU **Institute of / Graduate School of.....** student ID **……..**, successfully defended the **thesis/dissertation** entitled "…….**THESIS TITLE……..**", which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Gürkan HIZAL** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Metin Hayri ACAR** Istanbul Technical University	.....
	Prof. Dr. Nergis ARSU Yıldız Technical University	.....

Date of Submission : 06.05.2014
Date of Defense : 28.05.2014

To my dearest family,
I love y'all!!!

FOREWORD

This master study has been carried out at Istanbul Technical University, Chemistry Department of Science & Letter Faculty.
I would like to express my gratitude to my thesis supervisor, Prof. Dr. Gürkan HIZAL and co-supervisor Prof. Dr. Ümit TUNCA for offering invaluable help in all possible ways, continuos encouragement and helpful criticism throughout this research.
I would like to express my special thanks to, Assoc. Prof. Dr. Hakan DURMAZ, Res. Assist. Neşe ÇAKIR and Res.Assist. Ufuk Saim GÜNAY for their helpful and understanding attitudes during my laboratory and thesis study in ITU. It has been a pleasure to work with them. I would like to also extend my sincere gratitude to Pınar Sinem OMURTAG and Bilal Buğra UYSAL for their friendly and helpful attitudes and unbelievable sensibility during my laboratory works.
I would like to thank my colleagues Sümeyra YOLDAŞ, Burcu YILMAZ, Gökçe MİHLAÇ, Erhan DEMİREL, Hande TINAS , Lale ATICI, Meir ABUAF for their friendly and helpful attitude during my laboratory works.
I would like to dedicate the this thesis to my family Halil İbrahim PALAK, Şükran PALAK, Assist. Prof.Dr. Gökçe PALAK, Handan PALAK for their encouragement, support and especially for their parental guidance and endless devotion throughout my education and my life.

May 2014 Gizem PALAK

TABLE OF CONTENTS

Page

ABBREVIATIONS

^{1}H NMR **:** Hydrogen Nuclear Magnetic Resonance Spectroscopy
ATRP **:** Atom Transfer Radical Polymerization
CH_2Cl_2 **:** Dichloromethane
$CDCl_3$ **:** Deuterated chloroform
Et_3N **:** Triethylamine
EtOAc **:** Ethyl acetate
DMF **:** *N*,*N*-dimehthylformamide
DVB **:** Divinyl benzene
^{19}F NMR **:** Fluoro Nuclear Magnetic Resonance Spectroscopy
FPT **:**Freeze-Pump-Thaw
GC **:** Gas Chromatography
GPC **:** Gel Permeation Chromatography
MWD **:** Molecular Weight Distribution
NMP **:** Nitroxide Mediated Polymerization
PDI **:** Polydispersity Index
PMDETA **:** *N, N, N',N'', N''*-Pentamethyldiethylenetriamine
PPFS **:** Poly (pentafluorostyene)
PS **:** Poly(styrene)
RAFT **:** Reversible Addition Fragmentation Chain Transfer
St **:** Styrene
TD-GPC **:**Triple Detector-Gel Permeation Chromatography
THF **:** Tetrahydrofuran

LIST OF TABLES

Page

LIST OF FIGURES

Page

SYNTHESIS AND FUNCTIONALIZATION OF 3-ARM STAR POLYPENTAFLUOROSTYRENE VIA THIOL/PARA FLUORO CLICK REACTION

SUMMARY

Star polymers are branched polymers consisting of several linear chains linked to a central core. Among all branched structures, star polymers have been certainly the most investigated architectures, attracting much experimental and theoretical interest, due to their distinct properties in bulk, melt and solutions. İn contrast to lineer structures, star polymers often exhibit lower solution and melt. There are two general strategies used to produce star polymers: the arm-first and core-first techniques. In the arm-first strategy, a polymer with proper end-group functionality is reacted with an appropriate multifunctional core to give a star polymer. In the second strategy (core-first), the polymer chain is simultaneously grown from a multifunctional initiator. The revolution of free radical polymerization has led to development of controlled/‘‘living” radical polymerization (C/LRP) methods that have been facilitated the access to the construction of well-defined macromolecules without stringent requirements on the experimental conditions. Currently, three methods appear to be most efficient and can be successfully applied: nitroxide mediated radical polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition-fragmentation chain transfer (RAFT). Ultimately, their widespread acceptance and exploitation in polymer synthesis is justified by their seemingly unlimited potential to create a wide range of well-defined macromolecules with precise control over composition, architecture and functionality.

The term “click” refers to versatile, efficient, specific and energetically-favored chemical reactions, which could become universal tools first in synthetic chemistry lately extremely popular in polymer and materials science. Click reactions have brought a new sight to the green chemistry and also the reactions are not very difficult to make. By this way new functionally groups or polymer chains can be clicked to each other and give new topology.The most popular click reactions are the copper catalyzed azide–alkyne cycloaddition (CuAAC), Diels–Alder cycloaddition, thiol-ene, thiol-yne, and nitroxide radical coupling (NRC) reactions. These reactions have recently shown to be extremely powerful tools for advanced macromolecular design. Amoung the click reactions, thiol-ene click raction is considered the most encouraging the green aspects. This metal-free reaction can be performed in the absence of solvents in some cases, and can be photochemically controlled (even in the absence of a photoinitiator). Some stuedies have showed that the thiol-ene click reaction is more efficient when initiated by light than by thermally.

The development of fluoropolymers began with the invention of polytetrafluoroethylene (PTFE) in 1938 by Dr. Roy Plunkett of DuPont Company, continuing in 1992 when a soluble perfluoropoly-mer (Teflon® AF) was invented, while fluoroplastics polymerized in supercritical carbon dioxide were introduced in 2002. Besides these commercially important examples many other routes [1] toward fluorinated materials have been researched intensively by both academic and industrial teams. the emergence of various functional materials with notable

properties: biomaterials, surfactants, lubricants, insulators, ion con- ducting materials (e.g. for Li-ion batteries) and proton conducting materials (e.g. for membranes for fuel cells). A number of materials such as paints and coatings as well as materials for the optic and electronic industries have additionally been developed [2]. Aromatic and aliphatic fluorinated polymers are becoming more and more important and remarkable materials because of low energy surface, high thermal stability, wonderful chemical resistance, low flammability and low refractive indexes.
In this thesis, we prepare pentafluorostyrene and polypentafluorostyrene-co-polystyrene 3-arm star homo and co-polymer via ATRP using core first method. Then, 1-octanethiol is clicked via thiol/para fluorine click reaction.

ÜÇ KOLLU POLİPENTAFLUROSTİREN YILDIZ POLİMERLERİN SENTEZİ VE THİOL/PARA FLORO 'CLİCK' REAKSİYONLARI İLE MODİFİKASYONU

ÖZET

Yıldız polimerler birkaç lineer polimer zincirinin bir merkez çekirdeğe bağlı olduğu dallanmış yapılardır. Tüm dallanmış yapılar arasında, şüphesiz yıldız polimerler en çok araştırılan, deneysel ve teorik açıdan ilgi çeken yapılardır. Üstün özellikler gösteren ileri polimer malzemelerin sentezi konusunda yoğun çaba harcanmaktadır. Mekanik ve fiziksel özellikleri birarada bulundurmalarından dolayı blok kopolimerler ve yıldız polimerler en çok rağbet edilen ileri malzemelerdir. Çok geniş uygulama alanlarına rağmen, blok kopolimerlerin ve yıldız polimerlerin iyi-tanımlı olarak sentezlenmesi halen bir meseledir

Yıldız polimerlerin elde edilmesinde kullanılan iki genel yöntem vardır: kol öncelikli ve çekirdek öncelikli yöntemleri. Kol öncelikli yönteminde, uygun uç grup fonksiyonalitesine sahip polimer ona uygun çok fonksiyonlu bir çekirdekle yıldız polimer elde etmek için reaksiyona sokulur. İkinci yöntemde (çekirdek öncelikli) ise, polimer zinciri çok fonksiyonlu bir başlatıcıdan eşzamanlı bir şekilde büyümektedir.

Kontrollü kompozisyon ve yapılarda iyi tanımlanmış makromoleküllerin sentezi polimer biliminde yeni bir alan açan iyonik polimerizasyon yöntemlerinin gelişimine kadar kimyagerler için sorun olmuştu. Ancak, iyonik polimerizasyon araştırmalarının gelişimi zorlu işlem koşulları; yüksek saflık ve çeşitli fonksiyonel monomerlerle uyumsuzluk söz konusu olduğundan bazı ciddi engeller ile karşılaşmaktadır. Serbest radikal polimerizasyonu safsızlıklara daha toleranslıdır ve çok çeşitli vinil monomerlerinin polimerleştirilmesi yeteneğine sahiptir fakat en büyük dezavantajı iyonik polimerizasyondaki gibi polimer yapı ve fonksiyonalite kontrolünün aynı derecede mümkün olmamasıdır. Bu nedenle, kaydadeğer çabalar serbest radikal polimerizasyonunu kontrollü bir şekilde gerçekleştirmek için harcanmıştır. Serbest radikal polimerizasyonunundaki devrim herhangi bir zorlu deneysel koşul gereksinimleri olmayan, iyi tanımlanmış makromoleküllerin inşasına erişim kolaylığı sağlayan kontrollü/"yaşayan" radikal polimerizasyon (C/LRP) yöntemlerinin gelişimlerine yol açmıştır. Günümüzde, en etkili ve en sık kullanılan üç C/LRP yöntemi: nitroksit ortamlı radikal polimerleşmesi (NMP), atom transfer radikal polimerleşmesi (ATRP), ve tersinir eklenme-ayrılma zincir transfer polimerleşmesidir (RAFT). Sonuç olarak, bu yöntemlerin polimer sentezinde geniş bir yelpazede yaygın olarak kabulu ve yararlanılması iyi tanımlanmış makromoleküllerin kontrollü kompozisyon, yapı ve fonksiyonalitede yapılmasındaki sınırsız potansiyellerine dayanır. Monomerden kolaylıkla polimer elde etmeyi mümkün kılan L/CRP türlerinden biri ATRP olmuştur. ATRP'nin temeli, radikal oluşumu ve polimerizasyonun oluşan radikal üzerinden yürümesidir. Radikal polimerizasyonu birkaç monomerden yüzlerce monomere kadar polimerleşmeyi gerçekleştirebildiği gibi, su ortamında emülsiyon ya da süspansiyon polimerizasyonunu da mümkün kılar. ATRP'de kullanılan geçiş metallerinin

halojenli bileşikleri, redoks reaksiyonu ile indirgenip-yükseltgenerek, tersinir bir mekanizmayı meydana getirir.
İşte bu tersinir mekanizma ile polimer zincirleri neredeyse aynı anda meydana gelerek, düşük polidispersiteli polimerlerin eldesini sağlar.
Click kimyası hızlı, etkin, güvenilir ve seçici olmak gibi özelliklere sahip olmasının yanı sıra yeni ilaç araştırma ve biyokimya çalışmalarında geniş olarak kullanılır. Click kimyasında en popüler reaksiyonlardan biri Huisgen 1,3-dipolar siklik katılması reaksiyonudur. Oda sıcaklığında olan azid ve alkin nin reaksiyonunda Cu(I) kataliz olarak kullanılır. Bu reaksiyonun çok tercih edilmesinin sebebi reaksiyon şartlarının basit olması, yan ürün olmaması, verimin yüksek olması ve saflaştırmanın kolay olmasıdır. Modüler click reaksiyonları şu özelliklere sahip olmalıdır:
1) Yüksek verimli olması; eğer yan ürünler var ise, bu ürünlerin kromatografik olmayan yöntemlerle uzaklaştırılabilir olması.
2) Regioseçici ve stereoseçici olması,
3) Oksijen ve suya karşı hassas olmaması,
4) Ilımlı, çözücüsüz (veya sulu) reaksiyon koşullarında gerçekleşebiliyor olması,
5) Diğer bilinen organik sentez reaksiyonları ile uyumlu olabilmesi,
6) Çok çeşitli ve kolay elde edilebilen çıkış bileşiklerine karşı yatkın olabilmesi
Ayrıca click reaksiyonu yeşil kimyaya yeni bir bakış açısı getirmiştir ve reaksiyonlar kolaylıkla gerçekleşebilmektedir. Bu sayede, yeni fonksiyonel gup ya da polimer zinciri birbirlerine bağlanarak yeni bir topoloji meydana getirmişlerdir.. En yaygın kullanılan click reaksiyonları, bakır katalizli azid-alkin siklokatılma (CuAAC) reaksiyonu, Diels-Alder siklokatılma reaksiyonu, tiyol-en ve tiyol-in reaksiyonları ve nitroksit radikal kenetlenme reaksiyonlarıdır.
Tiyol-in click reaksiyonları ile tiyol bileşikleri polimer zincirinde bulunan üçlü bağ ile yapıya radikalik olarak bağlanılmaktadır. Thiol-ene click reaksiyonları termal yolla yapılabileceği gibi ışıkla da yapılabilmektedir. Işıkla gerçekleştirilen bu reaksiyonlarda ortama foto başlatıcılar konulmaktadır ve de mekanizma radikalik olarak yürümektedir. Işık altında gerçekleştirilen thiol-ene reaksiyonu, termale göre daha etkili olduğu çeşitli yayınlarda belirtilmiştir. Reaksiyon ortamında bulunan nem ya da hava reaksiyon üzerine pek olumsuz etki yapmazken; havanın oksijeni radikal oluşumunu artırıp reaksiyon verimini artırmaktadır. Herhangi bir metal bulunmaması bu reaksiyonunun yeşil kimyayı desteklemesini ortaya koymaktadır. Tiyol-in reaksiyonlarının bazı dezavantajları vardır. Bunlar; disülfit oluşumu ve coupling (radikallerin baş başa katılması) gibi yan reaksiyonlardır.
Floropolimerlerin gelişimi politetrafloroetilen(PTFE)nin DuPont Company den Dr. Roy Plunkett 1938 yılında buluşu ile başlamış ve ardından 1992 de perfloropolymer(Teflon® AF)bulunuşu ile devam etmiştir.Bu önemli ticari örneklerinin yanında florlanmış materyaller[1] hem akademik hem de endüstriyel alanda derinlemesine araştırılmaya başlanmıştır.Bu fonksiyonlu materyaller biomateryal, yüzey aktif madde, kayganlaştırıcı madde, yalıtkan madde, iyonik iletken materyaller(Li iyon bataryalar), proton iletken materyaller(membranlar ve yakıt pilleri için) gibi geniş özellikler göstermektedir. Optik ve elektronik endüstride örneğin boya ve kaplama materyallerinde giderek gelişmektedir [2].
Aromatik ve alifatik florlu polimerler düşük yüzey enerjisi, yüksek ısı kararlılığı, mükemmel kimyasal dayanıklılığı, düşük yanabilme özelliği ve düşük refraktif indeksi özelliği ie giderek artan ve dikkat çekici bir önem kazanmışlardır.
Bu çalışmada, brom uçlu üç kollu başlatıcıyı sentezlemek için, tris (4-hidroksfenil-ethan) 2-bromo isobutrilbromür ile reaksiyona sokulmuştur. 3 kollu yıldız polimer

polipentaflorostiren ve polistiren-ko-polipentaflorostiren üç kollu başlatıcı kullanılarak çekirdek öncelikli metod ile atom transfer radikal polimerizasyonu (ATRP) ile elde edilmiştir. Daha sonra elde edilen pentaflorostiren homo ve kopolimerleri thiol/para flor 'click' methodu ile 1-oktantiol bağlanmıştır. 3 kollu yıldız polimerlerin yapısı ve molekül ağırlığı ^{1}H NMR, ^{19}F NMR, GPC and TD-GPC ile analiz edilmiştir.

1. INTRODUCTION

Recently, interest in the synthesis of polymers with specific molecular architectures has increased substantially. Block, graft, star, gradient, hyper branched, and comb polymers and copolymers have been synthesized by various radical and ionic polymerization techniques. These unique macromolecular architectures have allowed a wide range of applications, including stabilization of colloids, modification of crystal growth, controlling of micelle formation, and generation of intelligent materials for new drug carrier systems [3].

Polymers with unique architectures, such as star polymers, palm-tree-shaped polymers, dumbbell-shaped polymers, and dendritic polymers, were synthesized by conventional radical polymerizations, cationic and anionic polymerizations, ring-opening polymerization, and coordination polymerization. Recent progress in controlled living radical polymerization, especially in atom transfer radical polymerization (ATRP), has provided a powerful tool of synthesizing well-defined polymers and for macromolecular design. Most importantly, the tolerance of functional groups and impurities makes ATRP a versatile tool for synthesizing complex polymer molecules [4].

Star polymers have a fascinating macromolecular architecture due to their unique properties that differentiate them from their linear counterparts, such as a smaller hydrodynamic volume and lower viscosity at a given molecular weight as a consequence of their compact structure and globular shape. To date, known synthetic strategies for the formation of star polymers can be generalized into three main categories: (1) “core-first”; (2) “arm-first”; and (3) “coupling onto”. The core-first technique involves the use of a multifunctional initiator. The arm-first technique involves the synthesis of preformed arms followed by reaction with a cross-linking agents usually by using a divinyl cross-linker. The third method is a slight variation of the arm-first technique, which involves the synthesis of preformed arms followed by reaction with a cross-linking agent. The “click chemistry” concept was introduced by Sharpless and co-workers in 2001 [5]. Selected reactions were classified as click chemistry if they were modular, stereospecific, wide in scope, resulted in high yields,

and generated only safe byproducts. Several efficient reactions such as copper (I)-catalyzed azide-alkyne cycloaddition (CuAAC), Diels-Alder (DA) cycloadditions, and thiol-ene and thiol-yne reactions can be classified under this term.

Fluorinated polymers have many desirable properties, including low surface energy, high optical clarity, low refractive index, and high UV, thermal, and chemical stabilities. Fluorinated polymers based on aromatic fluorocarbons have similar properties. For example, poly(2,3,4,5,6 -pentafluorostyrene) (PPFS) forms low dielectric constant films, with low surface energies as manifested by high water contact angles. PPFS is also more thermally stable and more resistant to photo oxidation than polystyrene. In addition, 2,3,4,5,6 -pentafluorostyrene (PFS) is readily polymerized under much milder conditions than the pressurized conditions required to produce aliphatic fluoro polymers by radical polymerization of most fluorinated olefins. PFS can be polymerized by anionic conventional radical, atom transfer radical, and γ-ray polymerizations and copolymerizations at atmospheric pressure, and by chemical vapor deposition and plasma polymerization [6]. These efforts have led to the emergence of various functional materials with notable properties: biomaterials, surfactants, lubricants, insulators, ion con- ducting materials (e.g. for Li-ion batteries) and proton conducting materials (e.g. for membranes for fuel cells). A number of materials such as paints and coatings as well as materials for the optic and electronic industries have additionally been developed. The outstanding contribution in the past decade of the controlled radical polymerization (CRP) methods [7] allowed for development of advanced well-defined copolymers with various architectures (block, star, dendritic, alternating or graft) having predictable molecular weights and low molecular weight distrubition [2].

In this thesis, bromide terminated tris initiator was synthesized by using tris (4-hydroxy-phenyl-ethane). In the first study, we prepare 3-arm star polypentafluorostyrene with tris initiator via atom transfer radical polymerization (ATRP) on the core-first method. Subsequently, poly(pentafluorostyrene)-based polymers are prepared that can be grafted via thiol/para- fluorine ‘‘click’’ reaction with 1-octanthiol. (Figure1.1)

In the second study, we prepare 3-arm star polystyrene-*co*-polypentafluorostyrene with tris initiator via ATRP using core first method. Then, ps-*co*-pfps 3-arm star

polymer is reacted with 1-octanethiol via thiol/para- fluorine ‘‘click’’ reaction. (Figure1.2)

The composition and molecular weight of 3- arm star polymers were characterized by ^{1}H NMR, ^{19}F NMR, GPC and TD-GPC.

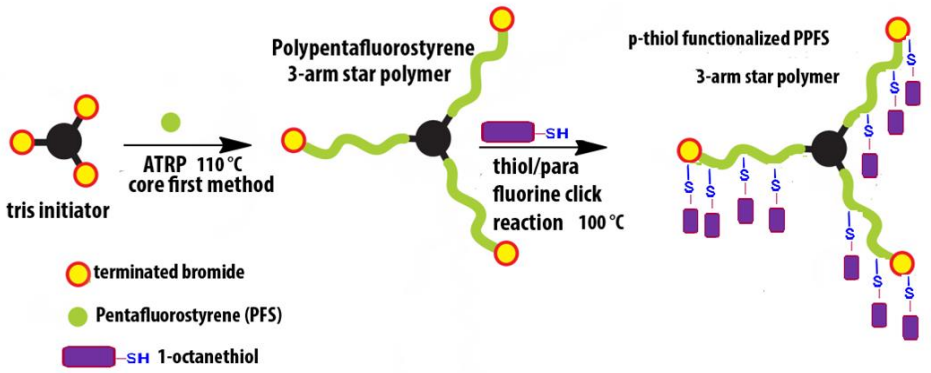


Figure 1.1 : General scheme for the synthesis and functionalization of 3-arm PPFS star polymer.

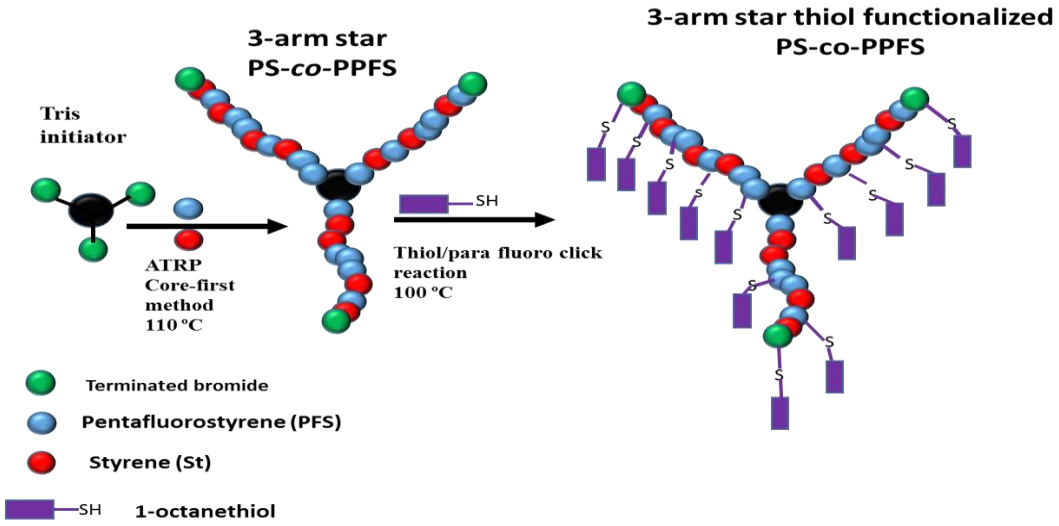


Figure 1.2 : General scheme for the synthesis and functionalization of 3-arm star PS-*co*-PPFS star polymer.

2. THEORETICAL PART

2.1. Controlled/ ‘‘Living” Polymerizations

Living radical polymerizations was started in the mid-1990s; radical polymerization was thought to be a mature process with relatively little left to discover. Chain polymerizations without chain-breaking reactions are called as living polymerization by Szwarc[8]. Well-defined polymers, can only be synthesized by living ionic polymerizations or controlled/ “living” radical polymerization (C/LRP) methods [9]. Until recently, ionic polymerizations (anionic or cationic) were the only living techniques that efficiently controlled the structure and architecture of vinyl polymers. These polymerization techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends but they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers [10]. Living or controlled/“living” polymerization techniques allow the synthesis of well- defined polymers with controlled molecular weight, polydispersities, and terminal functionalities. The polymerization proceeds until all of the monomer has been consumed, and further additions of monomer result in continued polymerization [11].

Living polymerization provides end-group control and enables the synthesis of block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with molecular weight (MW) control and narrow molecular weight distribution (MWD). To obtain well defined polymers the initiator should be consumed at early stages of polymerization and that the exchange between species of various reactivities should be at least as fast as propagation [12] [13] [14].

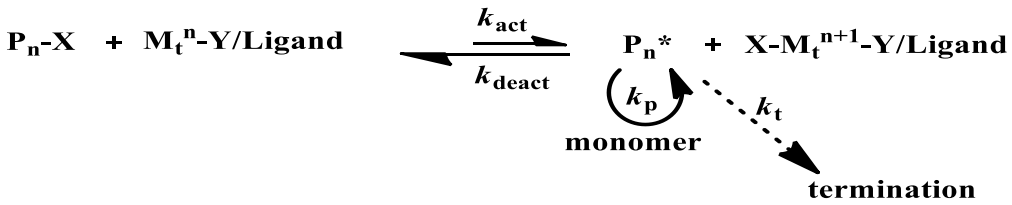
2.1.1. Control living radical polymerizations

Living free radical polymerizations have attained a tremendous following in polymer chemistry. A great deal of effort has been made to develop and understand different living free radical polymerization (LFRP) methods. Georges et al. first introduced true nitroxide mediated polymerization (NMP) in 1993, Matyjaszewski and

Sawamoto developed metal catalzed (Cu, Ru) living radical polymerization also called atom transfer radical polymerization (ATRP) in 1995, and Moad, Rizzardo and Thang reported reversible addition-fragmentation chain transfer polymerization (RAFT) in 1998 [15] [16] [17] [18].

2.1.1.1. Atom transfer radical polymerization (ATRP)

Atom transfer radical polymerization (ATRP) is a living radical polymerization process, which is consisting of the monomer, initiator, and catalyst composed of transition metal species with any suitable ligand. ATRP is one of the most convenient methods to synthesize well-defined low molecular weight polymers [19].



(2.1)

A general mechanism for ATRP is shown in Equation 2.1. ATRP is based on the reversible homolytic cleavage of carbon-halogen bond by a redox reaction. Homolytic cleavage of the alkyl (pseudo)halogen bond (RX) by a transition metal complex (activator, M_t^n –Y / ligand, where Y may be another ligand or a counterion) in the lower oxidation state generates an alkyl radical ($R^{\bullet}$) and a transition metal complex (deactivator, $X–M_t^{n+1}$ / ligand) in the higher oxidation state. The formed radicals can initiate the polymerization by adding across the double bond of a vinyl monomer, propagate, terminate by either coupling or disproportionation, or be reversibly deactivated by the transition metal complex in the higher oxidation state to reform the dormant species and the activator.

This process occurs with a rate constant of activation, k_{act}, and deactivation k_{deact}, respectively. Polymer chains grow by the addition of the free radicals to monomers in a manner similar to a conventional radical polymerization, with the rate constant of propagation, k_p. Termination reactions (k_t) also occur in ATRP, mainly through radical coupling and disproportionation; however, in a well-controlled ATRP, no more than a few percent of the polymer chains undergo termination. Typically, no more than 5% of the total growing polymer chains terminate during the initial, short, nonstationary stage of the polymerization. Other side reactions may additionally limit the achievable molecular weights.

ATRP generates oxidized metal complexes, the deactivators, which behave as persistent radicals to reduce the stationary concentration of growing radicals and thereby minimize the contribution of termination at later stages. A successful ATRP will have not only small contribution of terminated chains but also uniform growth of all the chains; this is accomplished through fast initiation and rapid reversible deactivation.

Since the deactivation rate constant is substantially higher than that of the activation reaction $K_{eq} = K_{act} / Kd_{eact}$ ~10-7; each polymer chain is protected by spending most of the time in the dormant state, and thereby the permanent termination via radical coupling and disproportionation is substantially reduced. K_{eq} must be low to maintain a low stationary concentration of radicals; thus, the termination reaction is suppressed [20] [21] [22]. Polydispersities in ATRP decrease with conversion, with the rate constant of deactivation and also with the concentration of deactivator. The molecular conversion and the amount of initiator used, DP = $\Delta[M]/[I]_0$; polydispersities are low, M_w / M_n <1,3. An ATRP system consists of the monomer, an initiator, and a catalyst composed of a transition metal species complexed with any suitable ligand [23].

Monomers

A variety of monomers, including styrene, acrylonitrile, (meth) acrylates, (meth) acrylamides, 1,3-dienes, and 4-vinylpyridine, undergo ATRP. The less reactive monomers, such as ethylene, vinyl chloride, and vinyl acetate, have not been polymerized by ATRP. Some other monomers may be difficult to polymerize since they exhibit side reactions. Monomers often have a major effect on the ATRP, several variables can account for the influence of the used monomer. For each monomer the rates of activation and deactivation (k_{act} and k_{deact}) are unique, and these in combination with the rate of propagation k_p determine the polymerization rate. The most common monomers in the order of their decreasing ATRP reactivity are methacrylates, acrylonitrile, styrenes, acrylates, (meth)acrylamides [24].

Initiators

Initiator efficiency is of prime importance for succesful ATRP. Generally, alkyl halides RX with resonance stabilizing substituents are efficient initiators for ATRP.

Often, the structure of the initiator is analogous to the structure of the halogenated polymer chain end to obtain similar reactivity of the carbon-halogen bond. For example, styrene polymerizations often incorporate 1-phenylethyl chlorides or bromides as the initiators [15]. In ATRP, alkyl halides are typically used as the initiator and the rate of the polymerization is first order with respect to the concentration of alkyl halides. To obtain well-defined polymers with narrow molecular weight distributions, the halide group X, must rapidly and selectively migrates between the growing chain and the transition-metal complex. Thus far, bromine and chlorine are the halogens that afford the best molecular weight control [25] [26] [27] [28]. Iodine works well for acrylate polymerizations; however, in styrene polymerizations the heterolytic elimination of hydrogen iodide is too fast at high temperatures. Fluorine is not used because the carbon–fluorine bond is too strong to undergo homolytic cleavage [29]. The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. The main role of the initiator is to determine the number of growing polymer chains. If initiation is fast and transfer and termination is negligible, then the number of growing chains is constant and equal to the initial initiator concentration. The theoretical molecular weight or degree of polymerization (DP) increases reciprocally with the initial concentration of initiator in a living polymerization [20].

Catalysts

Catalyst is the most important component of ATRP. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. There are several prerequisites for an efficient transition metal catalyst. An efficient catalyst should be able to expand its coordination sphere and oxidation number upon halogen abstraction from an initiator (alkyl halide) or dormant polymer chains. The metal center should have reasonable affinity toward a halogen. Additionally, the catalyst should not participate in any side reactions which would lower its activity or change the radical nature of the ATRP process [30].

A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. The majority of work on ATRP has been conducted using copper as the transition metal. Apart from copper-based complexes, iron, nickel, rhenium,

ruthenium, rhodium, and palladium have been used to some extent [31] [32] [33] [34]. Recent work from Sawamoto et al. shows that the Ru-based complexes can compete with the Cu-based systems on many fronts. A specific Fe-based catalyst has also been reported to polymerize vinyl acetate via an ATRP mechanism [35].

Ligands

The main role of the ligand in ATRP is to solubilize the transition-metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. The ligand should complex strongly with the transition metal, should also allow expansion of the coordination sphere, and should allow selective atom transfer without promoting other reactions. Nitrogen ligands have been used in copper- and iron-mediated ATRP. For copper- mediated ATRP, nitrogen-based ligands work particularly well. In contrast, sulfur, oxygen, or phosphorus ligands are less effective due to in appropriate electronic effects or unfavorable binding constants. For copper-based ATRP, the coordination chemistry of the transition-metal complex greatly affects the catalyst activity. The electronic ans steric effects of ligands are also important [20]**.**The most common ligands for ATRP systems are substituted bipyridines, alkyl pyridylmethanimines and multidentate aliphatic tertiary amines such as N,N,N′,N″,N″ pentamethyldiethylenetriamine (PMDETA), and tris[2-(dimethylamino) ethyl]amine (Me6-TREN**)** [15] [36]. In addition to those commercial products, it has been demonstrated that hexamethyltriethylene tetramine (HMTETA) provides better solubility of the copper complexes in organic media and entirely homogeneous reaction conditions [37] . Since copper complexes of this new ligand are almost insoluble in water, ATRP technique can be employed in preparing poly(acrylate esters) in aqueous suspensions [38] .

Solvents

ATRP can be carried out either in bulk, in solution or in a heterogeneous system (e.g., emulsion, suspension). Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol, water, carbon dioxide and many others have been used for

different monomers. A solvent is sometimes necessary especially when the obtained polymer is insoluble in its monomer [39].

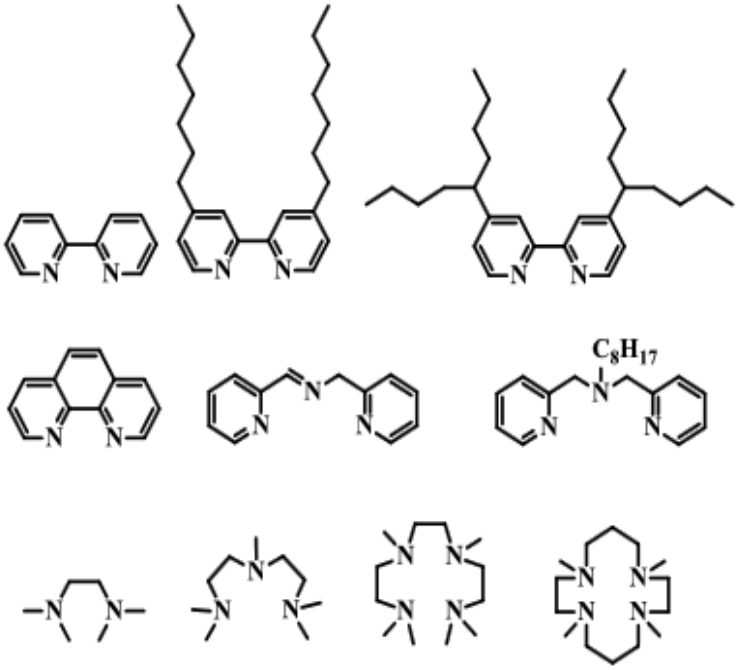


Figure 2.1: The most common ligands for ATRP system.

2.2. Click Chemistry

"Click chemistry" is a chemical term defined by Sharpless in 2001 and describes chemistry tailored to generate substances quickly and reliably by joining small units together [5]. Requirements for click reactions involving one or more polymeric reagents, which orginally defined by Sharpless, are high yields, stable compounds, modular, wide in scope, chemoselective, single reaction trajectory. There are other adapted requirements, which are related to synthetic polymer chemistry, like equimolarity, large-scale purification, fast timescale [40]. Nowadays there are several processes have been identified under this term in order to meet these criterias such as nucleophilic ring opening reactions; non-aldol carbonyl chemistry; thiol additions to carbon–carbon multiple bonds (thiol-ene and thiol-yne); and cycloaddition reactions. Among these selected reactions, copper(I)-catalyzed azide-alkyne (CuAAC) and Diels-Alder (DA) cycloaddition reactions and thiol-ene reactions have gained much interest.

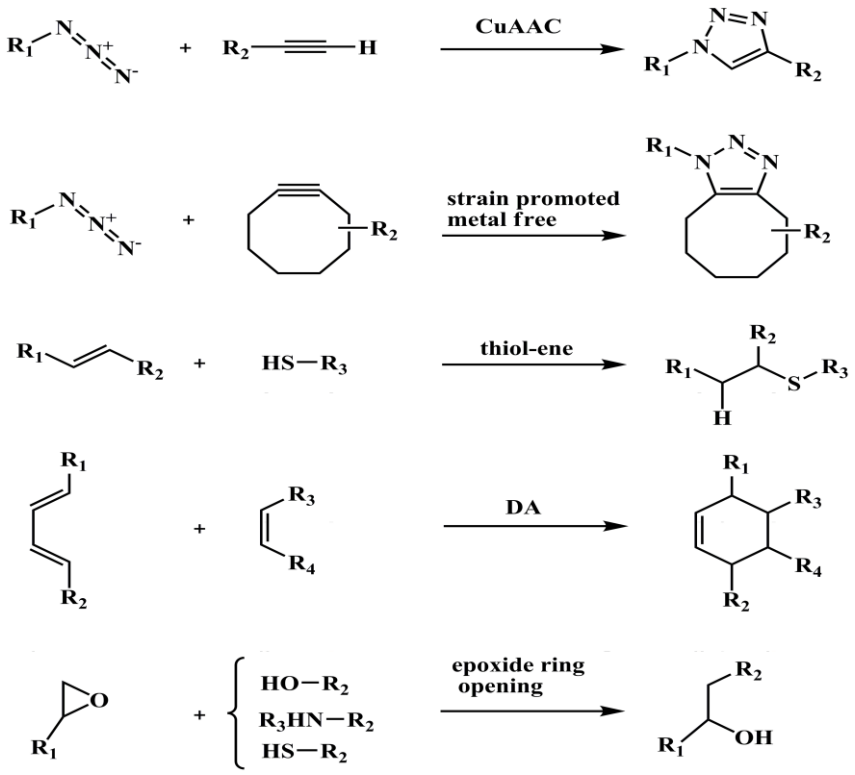
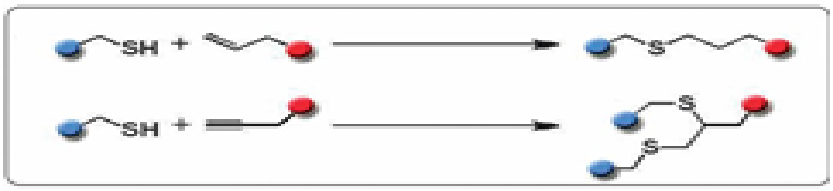


Figure 2.2: General represantion of click reaction.

2.2.1. Thiol-yne and thiol-ene reaction

The thiol-ene click reaction has realized between a thiol and an alkene to form a thioether linkage. More specifically, the sulfur–carbon bond formation follows an anti-Markonikov process that can be promoted by UV light radiation or by radical initiators.Thiol-ene click reactions are discovered in chemistry at early times, but have been rather extensively studied over the last century [41] [42] [43]. Thiol-ene click reaxtions depicted in1926 by Braun and Murjahn [44]. During the time that thiol-ene polymerizations utilize for the formation of networks [45] [46] or for the purpose of controlling molecular weight in radical polymerizations, thiol-ene reaction is more recently also referred to as a click reaction [47]. Additionally, TE reactions can proceed via two routes,anti-Markovnikov radical addition or base catalyzed Michael addition (MA). Hawker et al. demonstrated the use of TE ‘‘click’’ reactions for the formation of monodisperse dendrimers. Schlaad et al. successfully utilized this chemistry for the functionalization of 1,2-polybutadiene side groups, as well as poly(2-oxazoline)s bearing pendant alkene moieties. Other thiol based ‘‘click’’ reactions have been developed and can be listed as thiol–maleimide addition, thiol-isocyanate addition, pyridyl–disulfide exchange, and thiol–parafluoro.Thiol terminated polymers can be easily obtained by reversible addition–

fragmentation chain transfer (RAFT) polymerization of a wide range of monomers and a subsequent cleavage of the chain transfer agent. Alternatively, disulfide containing bifunctional ATRP initiators can be used for the preparation of thiol functionalized polymers [48].



(2.2)

Radicalic thiol-ene click proceeds by the same mechanism with chain transfer polymerization mechanism. Firstly, a thiyl radical is generated from a thiol-functionalized molecule by hydrogen abstraction from an initiator-derived radical, which subsequently reacts with carbon–carbon double bond. This is like propagation step. And then, the radical abstracts a proton from another thiol to form the reaction product and recover a thiyl radical (Figure 2.3). But unfortunately, thiol-ene chemistry has significant side reactions [49], the whole process may not be considered a click reaction, as this is a direct paradox to the click concept. Known side reactions are disulfide formation and head-to-head coupling of the carbon centered radicals. These two reactions are arguably the most prominent reactions terminating the thiol-ene cycle. Thus, thiol-ene may only serve as an efficient conjugation tool if such reactions can be largely avoided.

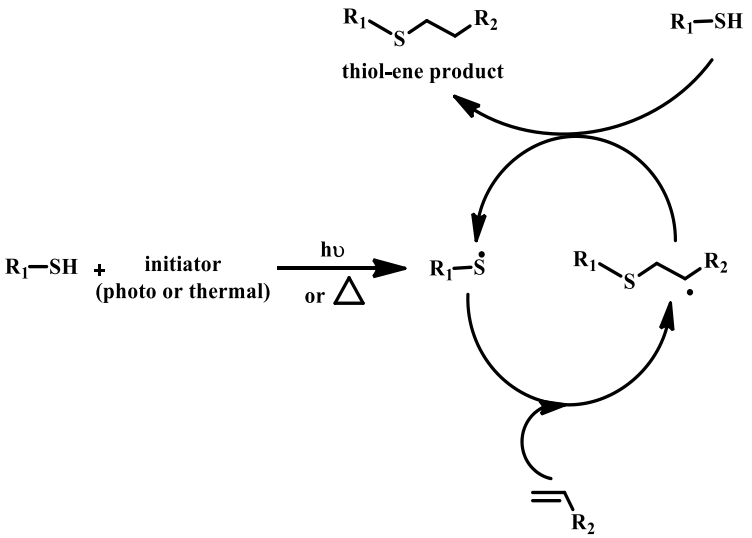


Figure 2.3: Presentation of Thiol-yne Reaction.

2.2.2. Thiol-para fluoro Click Reaction

Schubert et al. have shown a route that combines NMP and metal free click chemistry where well defined homopolymers of pentafluorostyrene (PFS) were functionalized by thiol-para fluoro click, as illustrated in Figure 2.4. The click reaction proceeded at ambient temperature in the presence of triethylamine as base and N,N-dimethylformamide as solvent. Moreover, the kinetics of the substitution reaction was monitored by measuring ^{19}F NMR spectra at 40ºC and quantitative conversions were observed in less than 1 h.

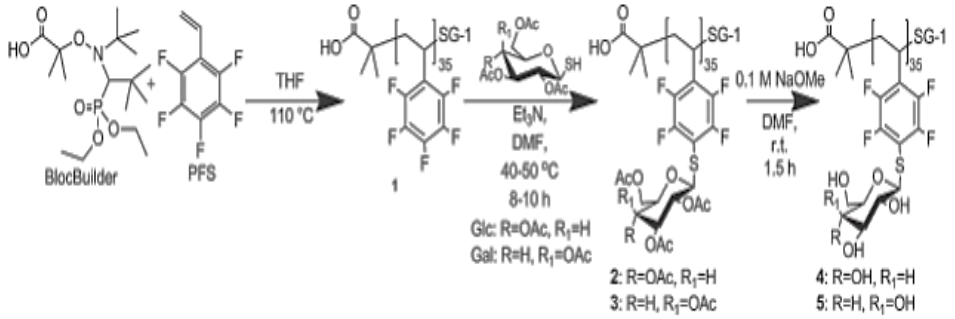


Figure 2.4: Schematic Representation of the Synthesis Route for the Preparation of Glycosylated Homopolymers.

Although in essence it is a nucleophilic substitution reaction, the versatility and efficiency of the amine or thiol substitution to the para position of C_6F_5 has been demonstrated by Schubert et al. to comply with most of the ‘‘click” chemistry requirements [50]. In addition, a wide range of primary amines and thiols, which can be efficiently reacted with – C_6F_5 groups, are commercially available. The accessibility of the – C_6F_5 groups however is rather limited; obstructing the scope and modularity of the reaction [51].

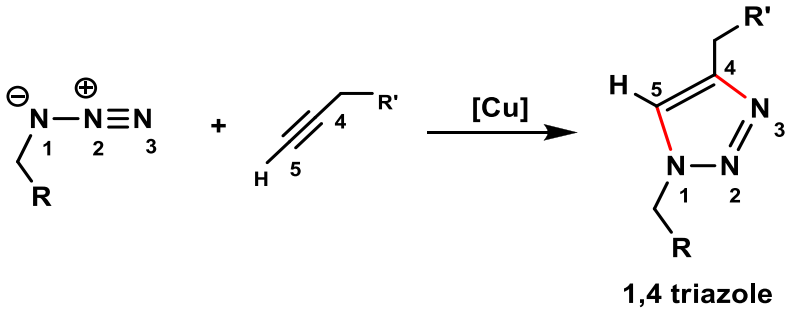
2.2.3. Copper(I)-catalyzed azide-alkyne cycloaddition (CuAAC)

The copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction is derived from the original 1,3-dipolar cycloaddition of organic azides to terminal alkynes discovered by Huisgen et al. [52] and later enhanced and popularized by Sharpless [5], as a very efficient coupling reaction. This methodology was also independently discovered by Meldal et al. [53] at about the same time that provides diverse applications ranging from small organic molecule synthesis, drug discovery to polymer and materials science. In recent years, triazole forming reactions have received much attention and new conditions were developed for the 1,3-dipolar

cycloaddition reaction between alkynes and azides [54]. 1,2,3-triazole formation is a highly efficient reaction without any significant side products and is currently referred to as a click reaction [55].

Copper(I)-catalyzed reaction sequence which regiospecifically unites azides and terminal acetylenes to give only 1,4-disubstituted 1,2,3 triazoles (Equation 2.3).

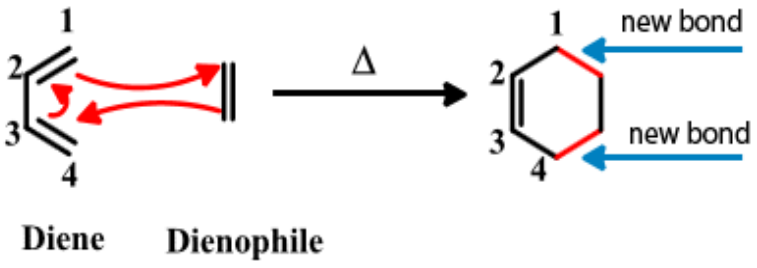
In fact, the discovery of Cu(I) efficiently and regiospecifically unites terminal alkynes and azides, providing 1,4-disubstituted 1,2,3-triazoles under mild conditions, was of great importance**.** On the other hand, Fokin and Sharpless proved that only 1,5-disubstituted 1,2,3-triazole was obtained from terminal alkynes when the catalyst switched from Cu(I) to ruthenium(II) [56].



(2.3)

2.2.4. Dials-Alder

The Diels-Alder reaction is a concerted [4π+2π] cycloaddition reaction of a conjugated diene and a dienophile to yield a 6-membered ring. This reaction is one of the most powerful tools used in the synthesis of important organic molecules. The three double bonds in the two starting materials are converted into two new single bonds and one new double bond to afford cyclohexenes and related compounds (Equation 2.4) [57] [58] [59] .



(2.4)

DA cycloaddition reaction forms not only carbon-carbon bonds but also heteroatom-hetroatombonds (hetero-Diels-Alder, HDA) and it is widely used synthetically to prepare siz-membered rings [60]. Typically, the DA reaction works best when either the diene is substituted with electron donating groups (like -OR, -NR2, etc) or when the dienophile is substituted with electron-withdrawing groups (like -NO2, - CN, -COR, etc) [61].

Some attractive features of DA reactions (retro-Diels-Alder, rDA) are thermal reversibility and decomposition reaction of the cyclic system that can be controlled by temperature [62].

In brief, DA "click" reactions show great potential for the prepration of tailor-made functional materials such as telechelic polymers, block, graft, star, star-block, H-shaped polymers, dendirimers, bioconjugates and hybris materials. DA "click" chemistry has some advantages such as water-solubility, high reaction yields, no detectable side-reactions and no requirement for additional catalysts [63].

2.3. Star Polymers

A star polymer consists of several linear polymer chains connected at one central core is one of the simplest form of branched topologies. Branching in polymers is a useful structural variable that can be used advantageously to modify polymer physical properties and the processing characteristics as a result of changing the melt, solution, and solid-state properties of polymers [64]. The presence of a central core in these macromolecules has lead to new, often improved characteristics, compared with their linear polymer analogs. The main feature of star polymers differing them from the linear analogues of identical molar masses, is their compact structure (smaller hydrodynamic volume and radius of gyration, and therefore lower viscosity) and the multiple functionality. This generates several potential applications for star polymers, including drug delivery, cosmetics, coatings, membrane, or lithography.

Based on the chemical compositions of the arm species, star polymers can be classified into two categories (Figure 2.6): homoarm (or regular) star polymer and miktoarm (or heteroarm) star copolymer [65] [66]. Homoarm star polymers consist of a symmetric structure comprising radiating arms with similar molecular weight

and identical chemical composition. In contrast, a miktoarm star molecule contains two or more arm species with different chemical compositions and/or molecular weights [67].

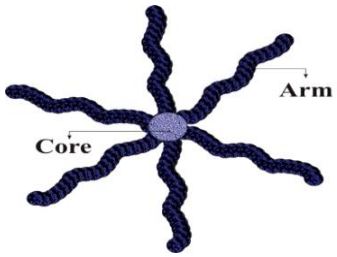


Figure 2.5: Illustration of a star polymer.

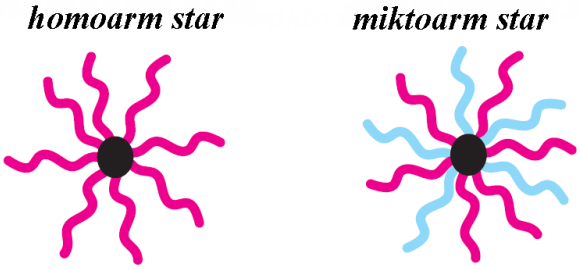


Figure 2.6: Illustration of star polymer categories.

Star polymers can be obtained using different polymerization methods, namely anionic polymerization, cationic polymerization, ring-opening polymerization (ROP) and a variety of C/LRP techniques including ATRP, NMP, and RAFT polymerization.

2.3.1. Preparation of star polymers

The methodology of living polymerization is ideally suited for the preparation of star polymers since it is possible to vary and control important structural paramethers such as molecular weight, molecular weight distribution, copolymer composition and microstructure, tacticity, chain end functionality and the number of branches per molecule. Because termination and chain transfer reactions are absent and the chain-ends may be stable for sufficient time periods, these polymerizations have the following useful synthetic attributes for star polymer synthesis:

I. One polymer is formed for each initiator molecule, so that the number average molecular weight of polymers or block segments can be predicted from the reaction stoichiometry. Multifunctional initiators with functionality *n* can form stars with *n* arms.

II. If the rate of initiation is rapid or competitive with the rate of propagation, polymers with narrow molecular weight distributions are formed [68].

III. When all of the monomer has been consumed, the product is a polymer with reactive chain ends that can be participate in a variety of post polymerization reactions:

a.block copolymerization by addition of a second monomer, and/or

b.end-linking with multifunctional linking agents to form the corresponding star polymers with uniform arm lengths.

Synthetic strategies for the construction of star polymers can be divided into three main categories according to their formation sequence of core and arms; (i) "core-first"; (ii) "arm-first"; and (iii) "coupling onto". Each of these approaches has associated advantages and disadvantages. The synthetic aspects of all approaches will be discussed in detail below.

2.3.1.1. Core-First Strategy

In the "core-first" strategy, the polymerization of monomer from the initiating functions present on the preformed multifunctional initiator (core) generates a star molecule with preserved initiating functions at the chain end of each arm, which can be further used for chain extension with a second monomer to form star block copolymers(Figure 2.7).

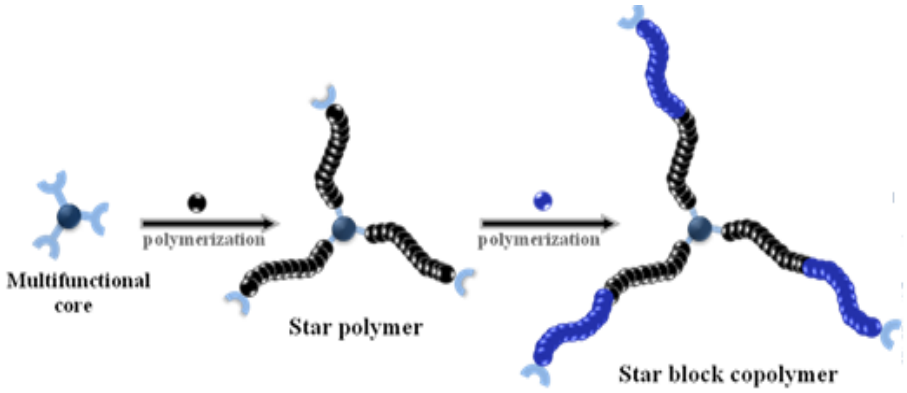


Figure 2.7: Schematic representation of the synthesis of star and star block copolymers by "core-first" strategy.

In the ''core-first'' method, there are several requirements that a multifunctional initiator has to fulfill in order to produce star polymers with uniform arms, low molecular weight distribution, and controllable molecular weights. All the initiation

sites must be equally reactive and have the same rate of initiation [65]. Aditionaly, broad molecular weight distribution was observed because of the large amounts of initiating sites and high probability of radical-radical recombination. Therefore, the polymerization is usually limited to low monomer conversion (<20%) to avoid the star-star coupling reaction [69].

2.3.1.2. Arm-First Strategy

In the "arm-first method", a star polymer is synthesized by crosslinking of linear arm precursors to form the core with cross-linking agents such as ethylene glycol dimethacrylate (EGDM) or divinyl benzene (DVB) [70] (Figure 2.8). While the "core-first" and "coupling onto" methods based on multifunctional initiators or cores with an accurate number of functional groups can afford star polymers with the desired number of arms, the arm-first with divinyl compounds of linear polymers results in statistically distributed numbers of arms due to occurring cross-linking reactions. However, the "arm-first" method can produce star polymers with a large number of arms (10-100) and consists of relatively simple procedures. This method is more practical than the "core-first" and "coupling onto" methods which require the complicated synthesis of the multifunctional agents.

Regardless of the linear arm precursors, the preparation of core cross linked star polymers by "arm-first" technique can be categorized into two broad strategies: macroinitiator and macromonomer (Figure 2.8).

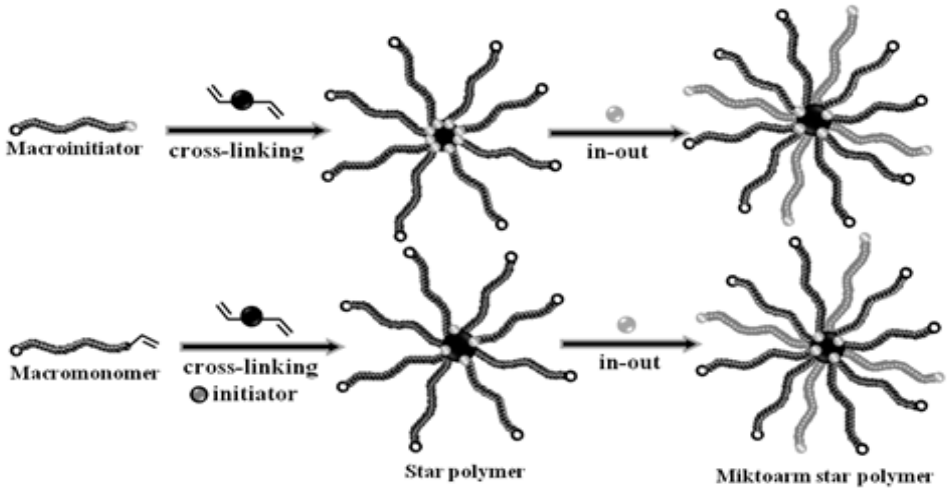


Figure 2.8: Schematic representation of the "arm-first" strategy for star polymer synthesis.

In the macroinitiator strategy, the star macromolecules formed by crosslinking linear macroinitiator, where both the initiating sites and the arms of the star molecule originate from the macroinitiator. A major drawback to star synthesis using linear macroinitiator as the arm precursor is that the star polymer usually have a broad polydispersity due to the significant level of star-star coupling reactions. When a linear macromonomer is employed to copolymerize with divinyl cross-linker by using a low-molar-mass initiator, the number of arms (derived from macromonomer) per star molecule is independently controlled. Thus, a low molar ratio of initiator to macromonomer decreases the number of initiating sites in the star core, which effectively limits the extent of star-star coupling reactions and results in star polymers with low polydispersity.

In addition, the further chain extension of the preserved initiating sites from the core to initiate the polymerization of another monomer will induce formation of miktoarm star polymer by the ‘‘in-out’’ method (Figure 2.8).

There are several parameters in an ATRP that should be controlled carefully in order to maximize the yield of stars and prevent star–star coupling reactions. The effects of type of cross-linker, cross-linker/macroinitiator molar ratio, macroinitiator DP, macroinitiator concentration, catalyst concentration, solvent nature, reaction temperature, and reaction time on the structure and yield of core cross-linked star polymers prepared via ATRP were investigated in several reports. The functionality of the stars prepared by this method can be determined by molecular weight measurements on the arms and the star product, but it is very difficult to predict and control the number of arms. The average number of arms attached to a star core depends on several experimental parameters, including the degree of polymerization (DP) and composition of the arm precursor, the chemical nature of cross-linker, the amount of cross-linker. Incomplete incorporation of linear arm precursors into the formed star is a common problem in this “arm-first” method, which could be explained by the loss of chain-end initiating sites or a buildup of steric hindrance around the core, as the coupling reactions proceed [31].

2.3.1.3. ‘‘Coupling-onto’’ Strategy

In the third ‘‘coupling onto’’ method, the linear arms of the star polymers are synthesized first followed by the coupling reactions between arms containing a reactive chain end group and a multifunctional coupling agent (core).

Monofunctional living chains of known length and low polydispersity are used as precursor. Subsequently, the active sites located at chain end are reacted with a compound carrying a number of appropriate reactive functions, whereupon chemical links are formed. The number of arms corresponds to the functionality of the linking agent as shown in Figure 2.9. The precursor chains become the star branches, and the linking agent becomes the core.

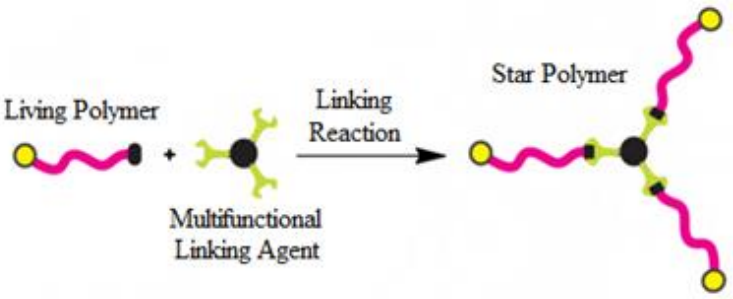


Figure 2.9: Schematic representation of the synthesis of star polymers by "coupling onto" method.

The most general and accurate way to prepare star homopolymers and block copolymers by anionic polymerization was the coupling of living polymers with multifunctional linking compounds. Several linking agents which are the chlorosilanes [71] and the chloromethyl or bromomethyl benzene derivatives [72] [73] have been used for the synthesis of star polymers. By using this method, star polymers with different arm numbers have been prepared [74] [75]. These model homopolymer and block copolymer stars are playing a critical role in the study of the relation between the architecture, the chain conformation, and the properties of the polymers. The main advantage of this method is that the arms of the resulting star polymer are well-defined because the precursor arms can be characterized independently from the star. Because of the well-defined arms, the number of arms can be readily determined by measuring the molecular weight of the star. In principle, a variety of well defined, star polymers with different numbers of arms can be prepared using this methodology by varying the functionality of the linking agents. Disadvantages of the method can be considered the sometimes long time required for the linking reaction and the need to perform fractionation in order to obtain the pure star polymer, since in almost all cases a small excess of the living arm is used in order to ensure complete linking.

2.4. (2,3,4,5,6)-Polypentafluorostyrene

In this thesis, 3-arm star 2,3,4,5,6-polypentastiren homo and copolymer are synthezied and functinalized. In the literature, it is mentioned that, a lot of scientists used some tecniques to synthesize and modifyed . These tecniques will shortly summarized by next examples.

According to Babiuch et al. , synthetic polymers offer the possibility to introduce biologically active moieties and to design tailor-made macromolecules with well-defined architectures and properties as shown in Figure 2.10. Glycopolymers, consisting of a synthetic polymeric backbone and pendant sugar moieties, are currently applied for affinity separations, bioassays, and biocapture analysis, in clinical diagnostics, as well as in targeted drug delivery systems. Chain length, size, composition, surface charge, and other properties of polymeric materials affect their recognition and uptake by cells and must be optimized to deliver polymers selectively to their target. However, it is often not possible to precisely modify selected properties without changing other parameters. To overcome these difficulties, well-defined poly(pentafluorostyrene)-based polymers are prepared that can be grafted via thiol/para- fluorine ‘‘click’’ reaction with 1-thio-b-D-glucose and 1-thio-b-D-galactose. Fluorescence micro- scopy and flow cytometry show that nanoparticles are taken up by $HepG_2$ cells to a higher degree than the respective water-soluble polymers, and that internalization of both galactosylated homo- and nanoprecipi- tated block copolymers is enhanced [76].

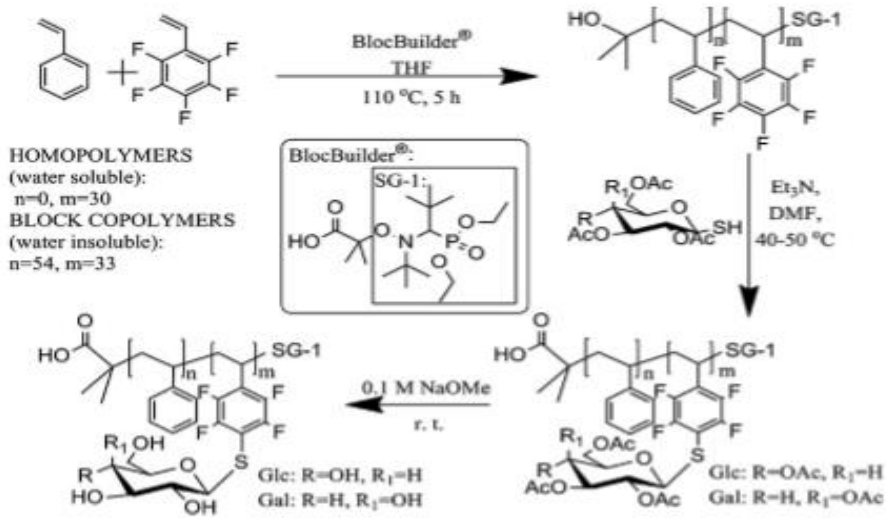


Figure 2.10: Schematic representation of the synthesis of the glucosylated and galactosylated homo and block copolymers.

Another study of Babiuch et al. shows that, water-soluble, gluco- sylated poly(pentafluorostyrene) derivatives revealed favorable coating material properties for magnetic iron oxide nanoparticles as shown in Figure 2.11. To prepare the coating material in high reproducibility and purity as well as in sufficient amounts, a new route of synthesis is established. The preparation and characterization of the glucosylated, tetrafluorostyryl monomer, bythiol-para fluorine "click" reaction, and its polymerization, via nitroxide-mediated radical process [77].

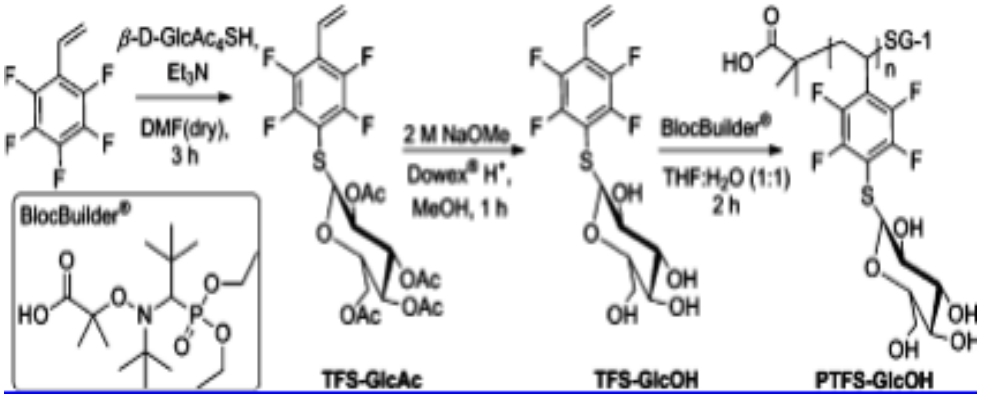


Figure 2.11: Schematic presentation of the synthesis of glucopolymer.

By Lou et al. , 2,3,4,5,6-Pentafluoro and 4-trifluoromethyl 2,3,5,6- tetrafluoro styrenes were readily copolymerized with methyl methacrylate (MMA) by a free radical initiator as shown in Figure 2.12. The copolymers were soluble in tetrahydrofuran and acetone. The films obtained were transparent and flexible. The glass transition temperatures (Tg_s) of the copolymers were found positively deviated from the Gordon–Taylor equation. The positive deviation could be accounted for by dipole–dipole intrachain interac- tion between the methyl ester group of MMA and the highly fluorinated aromatic moiety, which resulted in a decrease in the segmental mobility of the polymer chains and the enhanced Tg values of the copolymers [78].

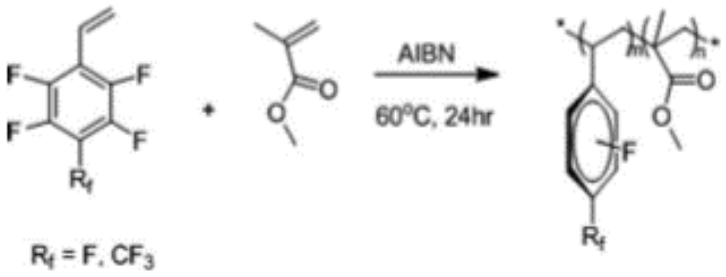


Figure 2.12: Synthesis of PMMA-co-poly(fluorinated styrene).

According to the study of Ying et al. , a series of highly fluorinated polymers were synthesized by copolymerization of 2,3,4,5,6-pentafluorostyrene (PFS) and fluorinated styrene derivate monomer (FSDM) as shown in Figure 2.13. A series of negative-type low-molecular-weight fluorinated photoresists (NFPs) were prepared by composing of fluorinated polystyrene derivates (FPSDs), diphenyl iodonium salt as a photoacid generator (PAG) and solvent. The polymer films prepared from NFP by photocuring exhibited excellent chemical resistance and thermal stabilities [79].

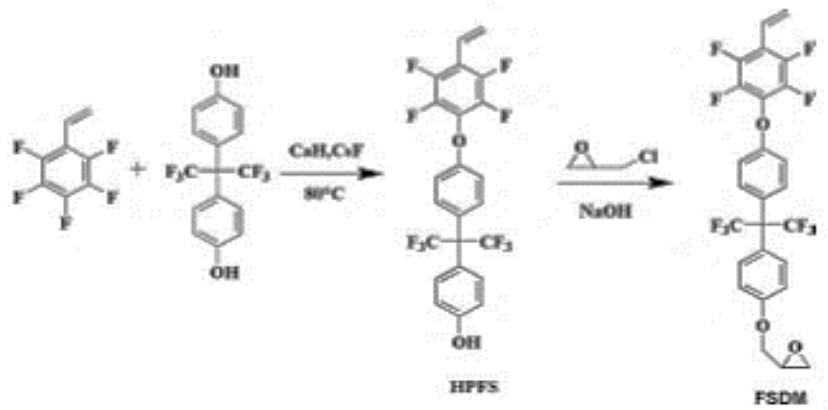


Figure 2.13: Synthesis of fluorinated styrene derivate monomer (FSDM).

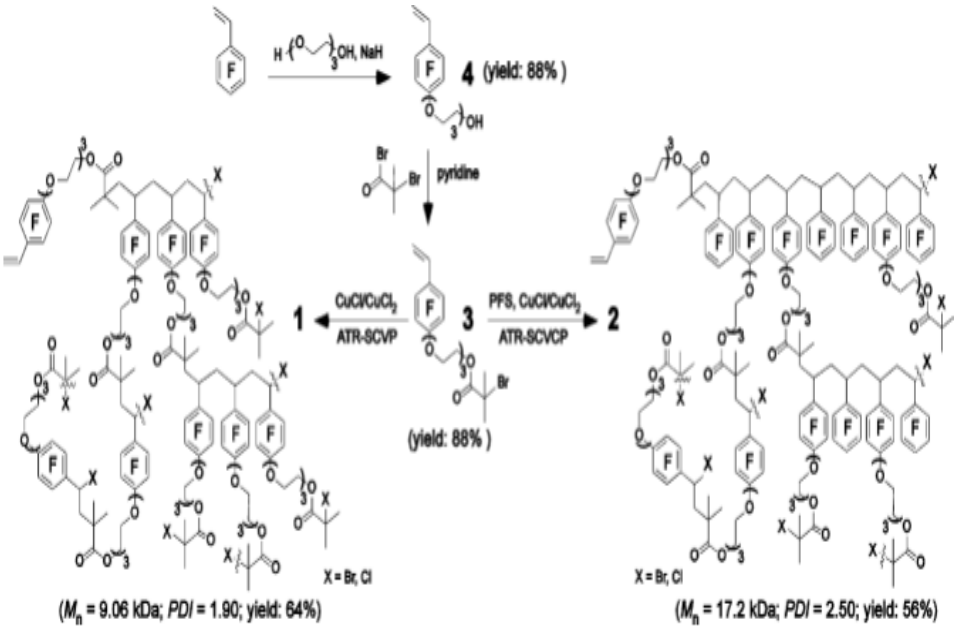


Figure 2.14: Syntheses of Hyperbranched Fluorohomopolymer 1 and Fluorocopolymer 2 by Atom Transfer Radical Vinyl Self-Condensing Vinyl (Co)polymerization.

By Kenya et al. , amphiphilic hyperbranched fluorohomopolymer and fluorocopolymer with tri(ethylene glycol) units incorporated at the molecular level

were synthesized by atom transfer radical self-condensing vinyl homopolymerization of an inimer, 4-[oxy(tri(ethylene glycol))bromoisobutyryl]-2,3,5,6-tetrafluorostyrene, and copolymerization of the inimer with 2,3,4,5,6-pentafluorostyrene (1:3, inimer:monomer), using 2,2′-bipyridine together with CuCl/CuCl2 as the ligand/catalyst/deactivator system as shown in Figure 2.14 [80].

Nitroxide-mediated radical polymerization has been used for the preparation of pentafluorostyrene (PFS) homopolymers and random copolymers of PFS and oligo(ethyleneglycol) methacrylate ($OEGMA_{8.5}$). By Becer et al., the poly(pentafluorostyrene) homopolymers were reacted with thiophenol at different ratios at room temperature in the presence of triethylamine as shown in Figure 2.15. The ‘‘clicked’’ polymers were characterized by ^{1}H and ^{19}F NMR spectroscopy and size exclusion chromatography. Moreover, the copolymerization kinetics of the PFS and $OEGMA_{8.5}$ copolymers was followed, and the phase transition behavior of random copolymers with different compositions was discussed [50].

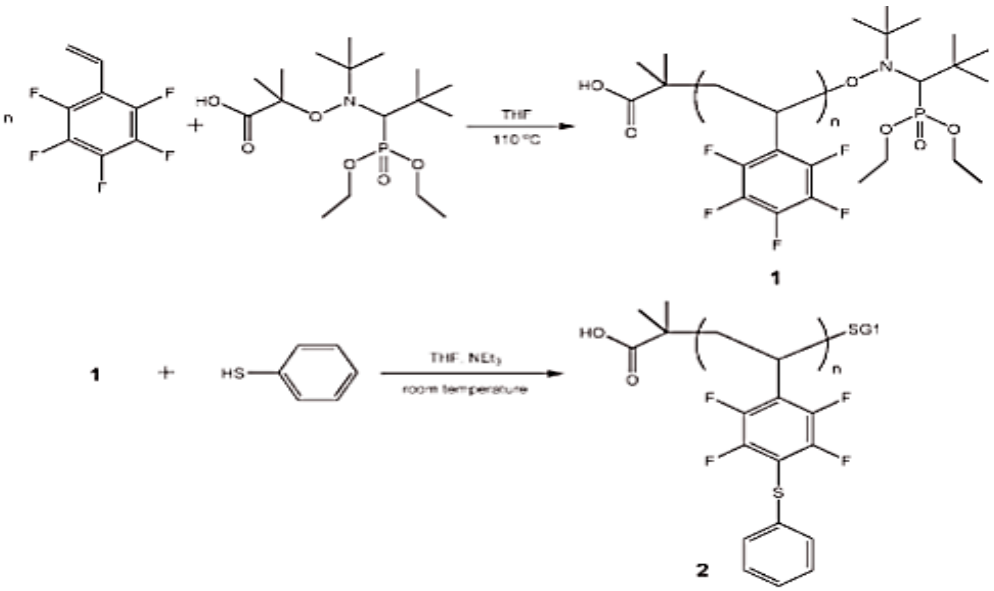


Figure 2.15: Schematic representation of the nitroxide-mediated polymerization of pentafluoros- tyrene initiated by Bloc Builder (top), thio-para fluoro ‘‘click’’ reaction on PPFS (bottom).

By Fu et al. , tadpole-shaped (or rod-coil) block-graft copolymers, consisting of a pentafluorostyrene polymer (PFS) block and a glycidyl methyacrylate polymer (PGMA) block with grafted poly(tert-butyl acrylate)(PtBA)side chains, or PFS-b-(PGMA-g-PtBA)copolymers, were synthesized by consecutive atom transfer radical polymerizations(ATRP’s).

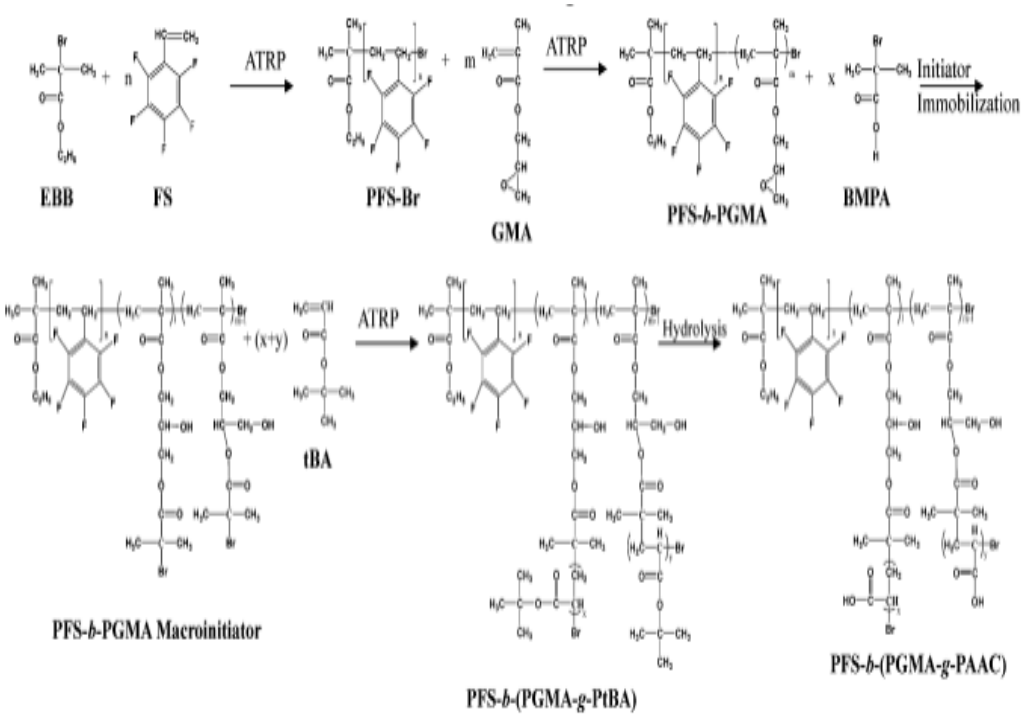


Figure 2.16: Consecutive Atom Transfer Radical Polymerizations (ATRP's) for the Preparation of the Block-Graft Amphiphlic Macromolecule of Poly(pentafluorostyrene)-block-(poly(glycidyl methacrylate)-graft-poly(acrylic acid)) (PFS-b-(PGMA-g-PAAC).

The process involved (i)synthesis of PFS via ATRP,(ii)synthesis of well-defined PFS-b-PGMA via ATRP, (iii) coupling of the bromoacid initiators with the glycidyl methacrylate units in the PGMA block to generate the PFS-b-PGMA macroinitiators, and (iv) ATRP- mediated graft copolymerization with tert-butylacrylate to generate the PFS-b-(PGMA-g-PtBA)copolymer as shown in Figure 2.16. Hydrolysis of the PtBA side chains in the block-graft copolymer into the acrylic acid polymer (PAAC) side chains gave rise to an amphiphilic PFS-b-(PGMA-g-PAAC) macromolecule with a brush-shaped hydrophilic head (rod) and a hydrophobic tail (coil) [4].

The preparation of sulfonate containing fluorinated block copolystyrenes have been developed by Ivaylo et al. based on initial ATRP of fluorinated styrene monomers as shown in Figure 2.17. The strategy depends on well-defined macrointiators that after conversion to block copolymers can be post functionalized in two steps with propylsulfonate groups in different ratios. The thermal investigations have demonstrated that addition of a PFS block to the sulfonate containing block improves the materials' thermal stability. After conversion to sulfonic acids the block copolymers became even more thermally stable [81].

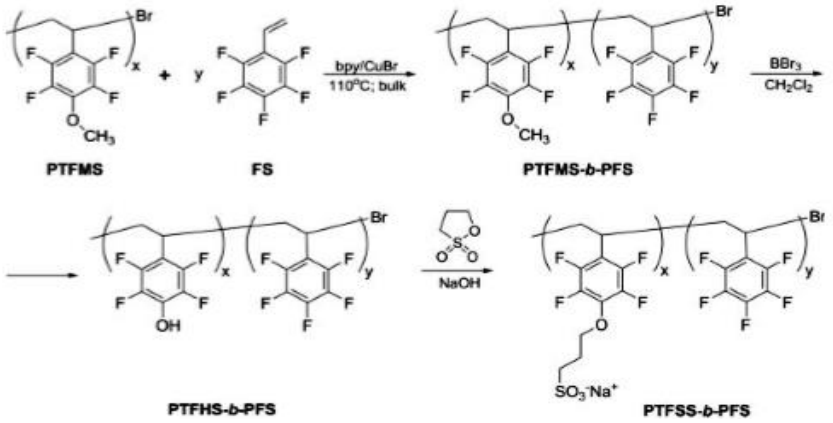


Figure 2.17: Preparation of sulfonated fluorinated block copolymers.

The study of Atanasov at al. shows that , highly protonogenic-functionalized polymers are considered as suitable ion conductors in fuel cell technology. The synthesis and conductivity of highly phosphonated polypentafluorostyrene are demonstrated. Efficient postphosphonation (90%) was achieved via the classical nucleophilic aromatic substitution (SNAr) MichaelisArbuzov reaction of polypentafluorostyrene (PFS) with tris(trimethylsilyl) phosphite as shown in Figure 2.18. The contrivance is in the cumulative electron-withdrawing effect of the fluorine functions. This polymer showed outstanding resistance to oxidative and thermal treatment (T_{decomp}= 340ºC at 70 %O_2 atmosphere).All this makes the phosphonated PFS a very promising candidate as polymer electrolyte for fuel cell applications[82].

Figure 2.18: Postphosphonation of PFS with TSP Followed by Complete Hydrolyzation of the Silyl Ester Derivative.

Munoz-Bonilla et al. describe the preparation of fluorinated microspheres by precipitation polymerization and their use to fabricate superhydrophobic surfaces. For that purpose, two different approaches have been employed. In the first approach, a fluorinated monomer (either 4-fluorostyrene or 2,3,4,5,6-pentafluorostyrene) was added to the initial mixture of monomers constituted by styrene (S) and divinylbenzene(DVB). The second approach is based on the

encapsulation of a block copolymer, polystyrene-b-poly(2,3,4,5,6-pentafluorostyrene), during the polymerization of the monomers (S and DVB), thus enabling the formation of particles with perfluorinated chains instead of single functional groups at the interface as shown in Figure 2.19 [83].

Rodriguez-Hernandez et al. describe the preparation, by precipitation copolymerization, of multifunctional divinylbenzene-co-pentafluoro- styrene microspheres able to produce superhydrophobic surfaces or disperse in aqueous media upon annealing either in air or water, respectively.

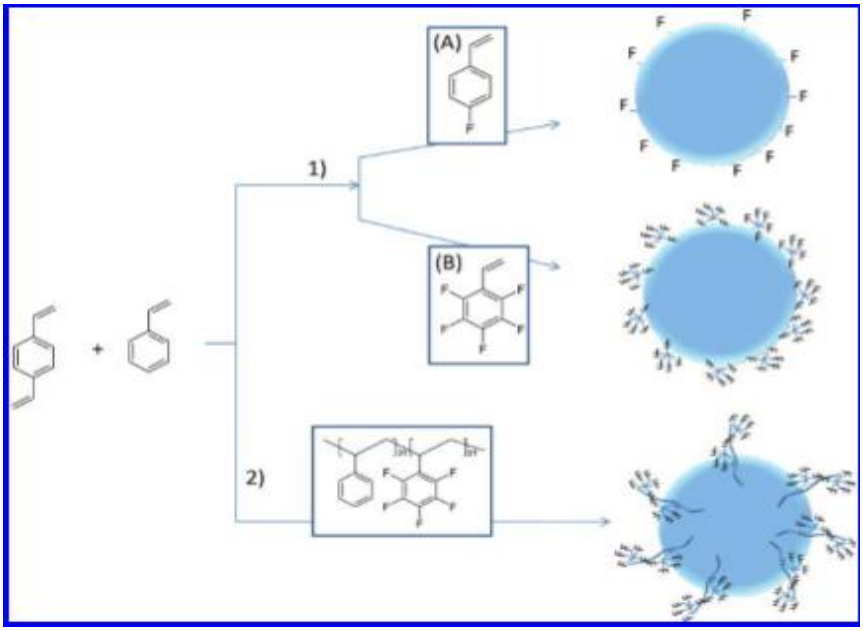


Figure 2.19: Approaches employed for the synthesis of particles containing fluoro moieties at the interface: (1) using either 4-fluorostyrene (A)or 2,3,4,5,6-pentafluorostyrene (B) as comonomer;(2) by encapsulation of a copolymer polystyrene-b-poly(2,3,4,5,6-pentafuorostyrene).

For that purpose, an amphiphilic block copolymer, polystyrene-b-poly(acrylic acid), was introduced in the initial feed composed of divinylbenzene and 2,3,4,5,6-pentafluorostyrene as shown in Figure 2.20 As a result, fluorinated particles were obtained in which the diblock copolymer was encapsulated during the polymerization step. Upon annealing in dry air, the particles are completely hydrophobic and form superhydrophobic surfaces. On the contrary, annealing in water induces the reorientation of the PAA groups toward the particle interface, thus the particles can be dispersed in aqueous media. In addition, the presence of carboxylic acid groups at the particle interface permits us to switch the surface charge between negative and neutral depending on the environmental pH [84].

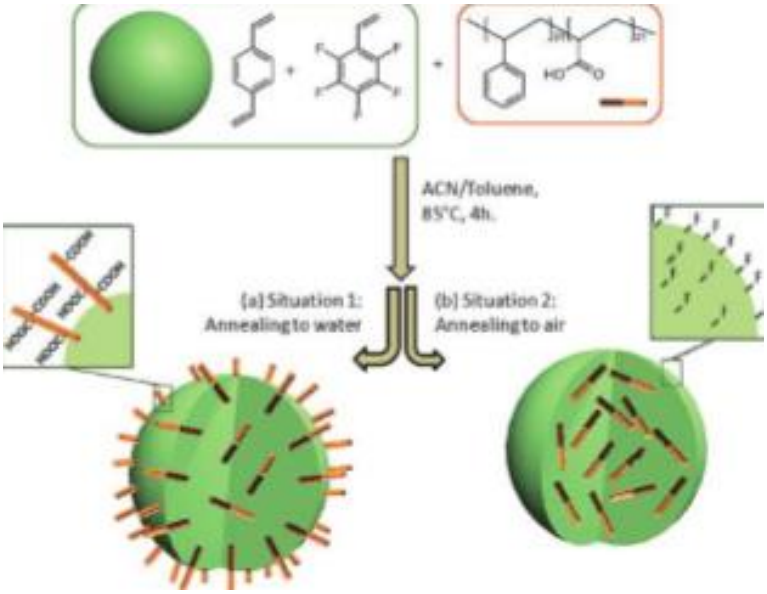


Figure 2.20: Approach to the preparation of environmentally responsive particles by combining hydrophobic moieties (fluorinated monomer) and hydrophilic functional groups (carboxylic acid groups present in the poly(acrylic acid) block).

3. EXPERIMENTAL WORK

3.1. Materials

Styrene (St, 99%, Merck) was passed through basic alumina column to remove inhibitor and then distilled from CaH_2 in vacuum prior to use. *N*, *N*, *N*', *N*'', *N*''-pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled over NaOH prior to use. 2,3,4,5,6-Pentafluorostyrene (PFS, 99%, Aldrich), 1-octanethiol (98.5%, Aldrich), 2-bromoisobutryl bromide (98%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acros), triethylamine (99.5%, Aldrich), 1,1,1-tris(4-hydroxy-phenyl-ethane)(99& Aldrich), CuBr (99.9%, Aldrich), $CuBr_2$ (99.9%, Aldrich), were used as received. Tetrahydrofuran (THF; 99.8%, J.T. Baker) was dried and distilled over benzophenone-Na. Anisole(99.7%, Aldrich), *N*,*N*-Dimethylformamide (DMF, 99.8%, Aldrich), methanol (99.8%, Aldrich) were used without further purification. Ethyl acetate (EtOAc) and hexane were in technical grade and distilled prior to use.

3.2. Instrumentation

Nuclear magnetic resonance spectroscopy (NMR)

^1H NMR measurements were recorded in $CDCl_3$ with $Si(CH_3)_4$ as internal standard, using an Agilent VNMRS 500 MHz instrument.

UV-visible spectrophotomether (UV-vis)

UV spectra were recorded on a Shimadzu UV-1601 spectrophotomether in CH_2Cl_2.

Gel permeation chromatography (GPC)

The conventional Gel Permeation Chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) consisting of a pump, refractive index, and UV detectors. Four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diamether, 300 mm length, packed with 5 μm particles) were used in series. The effective molecular weight ranges were 2000- 4.000.000, 50-100.000, 500-30.000, and 500–20.000, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at 30 °C. Toluene was used as an internal standard. The

molecular weights of the polymers were calculated on the basis of linear PS standards (Polymer Laboratories).

Triple detector gel permeation chromatography (TD-GPC)

The second GPC system with an Agilent model isocratic pump, four Waters Styragel columns (guard, HR 5E, HR 4, HR 3, and HR 2), a Viscotek TDA 302 triple detector (RI, dual laser light scattering (LS) (λ = 670 nm, 90° and 7°) and a differential pressure viscomether) (TD-GPC) was conducted to measure the absolute molecular weights in THF with a flow rate of 0.5 mL/min at 35 °C. All three detectors were calibrated with a PS standard having narrow molecular weight distribution (M_n = 115,000 g/mol, M_w/M_n = 1.02, [η] = 0.519 dL/g at 35 °C in THF, d*n*/dc = 0.185 mL/g) provided by Viscotek Company. Typical sample concentrations for GPC-analysis were in the range of 2–8 mg/mL depending on molecular weight of analyzed polymers. Data analyses were performed with OmniSec 4.5 software from Viscotek Company.

3.3. Synthesis Methods

Tris initiator Ethane-1,1,1-triyltris(benzene-4,1-diyl) tris(2-bromo-2-methylpropanoate) **(1)**, Poly[2,3,4,5,6 pentafluorostyrene](PPFS) 3-arm star polymer via ATRP **(2)**, Thiol/para click reaction PPFS with octanethiol **(3)**, Polystyrene (PS)-*co*-PPFS 3-arm star co-polymer **(4)**, Thiol para/click reaction of PS-*co*-PPFS 3-arm star co-polymer with octanethiol**(5)**.

3.3.1. Synthesis of tris initiator ethane-1,1,1-triyltris(benzene-4,1-diyl) tris(2-bromo-2-methylpropanoate)

1, 1, 1- tris (4- hydoxy-phenyl)ethane (1.0 g, 3.26mmol) was dissolved in dry 100 mL of THF in the 250 mL of round bottom flask. Et_3N (2,72 mL ,19,5 mmol) was then added into the reaction mixture. After stirring to 5 min, DMAP (0,398 g, 3.26 mmol) was added to the reaction medium, then cooled 0 ºC. 2-bromoisobutryl bromide (1,81 mL, 14.6 mmol) was added on 50 mL of THF in the dropwise. The mixture was stirred at 0ºC, then it stayed at the room temprature overnight. The salt was filtered off, and the solvent was evaporated under reduced pressure. The remaining residue was extracted with CH_2Cl_2, and organic phases dried over Na_2SO_4.

Excess CH_2Cl_2 was evaporated under reduced pressure. The remaining residue was crystallized in the ethyl acetate to give white crystal product.

Yield: 0.02g (74%) ^{1}H NMR ($CDCl_3$, δ) 7.16 (d, 6 Ar*H*) 7.07(d, 6 Ar*H*) 2.19(s, 3H, CH_3) 2.08 (s, 18 H, $C(CH_3)_2$-Br)

3.3.2. Synthesis of 3-arm PPFS star polymer

Tris initiator **(1)** (0.027g, 36.7µmol) and PFS monomer (3mL 0.022 mol), PMDETA (23µL, 0.11 mmol), anisol (3mL) were added to a 25 mL of Schlenk tube. CuBr (0.016g, 0.11 mmol) and $CuBr_2$ (0.005 g 0,022 mmol) were charged to the Schlenk tube**.** And then, the reaction mixture was degassed by three FPT cycles and left in vacuum and placed in a thermo stated oil bath at 110 ºC for 15 minutes. After the specified time, the polymerization mixture was diluted with THF, and passed through a column of neutral alumina to remove catalysts. THF was evaporated under reduced pressure, and star polymer precipitated into methanol. The polymer was dried in a vacuum oven at 40 °C.

Yield: 0.3 g (7.11 %) ^{1}H NMR ($CDCl_3$, δ) 7.02-6.80 (br, Ar*H* of phenyl groups), 2.75-2.42 (br, C*H*-PFS), 2.01 (bs, CH_2 next to the CH-PFS repeating unit), 1.57-1.27 (broad signal, initiator protons of CH_3C and O=CC(CH_3)$_2$).

^{19}F NMR ($CDCl_3$, δ) -161.10 (broad signal, meta- F) -154.23 (broad signal, para- F) -143.30 (broad signal, ortho-F)

3.3.3. Thiol/para- fluorine ‘‘click’’ reaction with 1-octanethiol of PPFS star polymer

In the first study, PPFS 3-arm star polymer (0.1 g, $1.26x10^{-2}$ mmol $M_{n,GPC}$: 7888) was added to a 250 mL round bottom flask with 150 mL THF. Then, Et_3N (0.2 mL 1.67mmol) and 1-octanethiol (0.1mL 0.7mmol) were added to the reaction at 50 °C for overnight. Then, polymer was precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 ^{o}C, but ^{1}H NMR and ^{19}F NMR result show that thiol/para fluorine click reaction did not occur under these reaction conditions. In the second experiment, 3-Arm PPFS star polymer (0.1 g, $1.26x10^{-2}$mmol $M_{n,GPC}$: 7888) was added to a 25mL of round bottom flask with 5 mL DMF. Then, Et_3N (1.16 mL 8.36 mmol) and 1-octanethiol (1.45 mL 8.36 mmol) were charged to the reaction

mixture placed in a thermostated oil bath at 100 °C for overnight. Then, polymer was precipitated in methanol. The polymer was dried for 24 h in a vacuum oven at 40 ^{o}C.

Yield: 0.08 g (80%) ^{1}H NMR ($CDCl_3$, δ) 7.12-6.60 (br, Ar*H* of PS), 2.97(t, CH_2S), 2.24-2.09 (br, C*H*-PFS), 1.88 (bs, CH_2 next to the C*H*-PFS), 1.46 (br, (CH_2)$_6$-CH_3 next to the CH_2S), 0.91(br, initiator protons of CH_3C and O=CC(CH_3)$_2$)

^{19}F NMR ($CDCl_3$, δ)- 142.52(ortho of PPFS+ meta F of p-thiol functionated PPFS) -134.36(ortho F of p-thiol functionated PPFS) -99.01 and -108.69 (broad signal, para and meta-F of PPFS)

3.3.4. Synthesis of PS-*co*-PFPS 3-arm star co-polymer

Tris initiator **(1)** (0.06g, 8.06x10^{-2} μmol) and PFS monomer (0.6 mL, 4.4 mmol), styrene (5mL, 0.044 mol) were added to a 25mL of Schlenk tube. Then, anisol (5mL) and PMDETA (50 μL, 24.18x10^{-2} mmol) and CuBr (0.034g, 24.18x10^{-2} mmol) were charged to the reaction mixture. The reaction mixture was degassed by three FPT cycles and left in vacuum and placed in a thermostated oil bath at 110 ^{o}C for 1 hour. One hour later, the polymerization mixture was diluted with THF, passed through a column of neutral alumina to remove cupper catalysts. Excess THF was evaporated under reduced pressure, and star polymer precipitated into methanol. The polymer was dried in a vacuum oven at 40 °C.

Yield: 0.7 g (13%) ^{1}H NMR ($CDCl_3$, δ) 7.10-6.10(br, aryl protons of PFS), 4.49(C*H* next to Br), 2.70(br, CH_2-C*H*-PS), 2.37 (bs, CH_2 next to CH-PFS) 2.07(br, C*H*-PFS), 1.93-0.94 (br, initiator protons)

^{19}F NMR ($CDCl_3$, δ) -163.09 (broad signal, meta-F) -158.45(broad signal, para-F) -141.60 (broad signal, ortho-F)

3.3.5. Thiol/para- fluorine ‘‘click’’ reaction with 1-octanethiol of PS-*co*-PPFS 3-arm star polymer

In the first experiment, PS-*co*-PFPS star co-polymer (0.1 g, 8.82x10^{-3} mmol $M_{n,GPC}$: 11327) was dissolved by 150 mL THF in the 250 mL round bottom flask. Et_3N (0.37 mmol 51 μL) and 1-octanethiol (0.154 mmol 27 μL) was added to the reaction at

60°C using the reflux system for overnight. Then, the polymer was precipitated in methanol. However, thiol/para fluoro click reaction did not occur in this reaction.

In the second experiment, we changed the solvent and used DMF. PS-*co*-PFPS star *co*-polymer (0.1 g, $8.82x10^{-3}$ mmol $M_{n,GPC}$: 11327) was dissolved by 3mL DMF in the 25 mL round bottom flask. Et_3N (0.37 mmol 51 μL) and 1-octanethiol (0.154 mmol 27 μL) was added to the reaction mixture in the oil bath at 50°C for overnight. Then, polymer was precipitated in methanol and was dried for 24 h in a vacuum oven at 40 ^oC. However, in this reaction we did not have an efficient result in ^{1}HNMR and ^{19}F NMR analysis.

In the third experiment, PS-*co*-PPFS 3-arm star polymer (0.1 g, $8.82x10^{-3}$ mmol $M_{n,GPC}$: 11327) was added to 25 mL of round bottom flask and dissolved in 5 mL DMF. Then, Et_3N (258 μL 1.85 mmol) and 1-octanethiol (322 μL 1.85 mmol) were put in the reaction and placed in a thermostated oil bath at 100°C overnight. Then, the polymer was precipitated in methanol and was dried for 24 h in a vacuum oven at 40 ^oC.

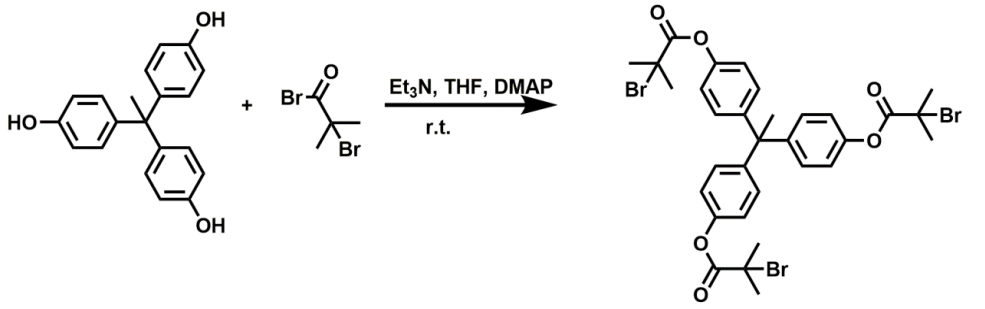
Yield: 0.07 g (70%) ^{1}H NMR ($CDCl_3$, δ) 7.06-6.59 (br, Ar*H* of PS), 2.82 (br, CH_2S), 2.40 (br, C*H*-PFS), 2.07 (br, CH_2 next to CH-PFS), 1.56(br, CH_2-C*H*-PS), 1.44(br, CH_2CH_2CH_2 next to CH_2S), 1.31 (bs, CH_2CH_2CH_2CH_3 of the end group of octanthiol), 1.09-0.91(br, protons of initiator)

^{19}F NMR ($CDCl_3$, δ) -141.44 (broad signal, meta-F of p-thiol functionated PS-*co*-PPFS) -135.42(broad signal, ortho-F of p- thiol functionated-PS-*co*-PPFS).

4. RESULTS AND DISCUSSION

4.1. Synthesis of Initiator

First of all, 1, 1, 1- tris (4- hydoxy-phenyl) ethane and 2-bromoisobutryl bromide were reacted in THF at 0ºC then, stayed overnight at room temperature to give **1** Equation 4.1. Thus, the initiators with proper functionalities for ATRP reaction were first prepared.



(4.1)

1

The ^{1}H NMR spectrum of 1 showed aryl protons at 7.15-7.06 ppm, methyl proton next to aryl protons at 2.19 ppm, methyl protons next to Br at 2.08 ppm (Figure 4.1).

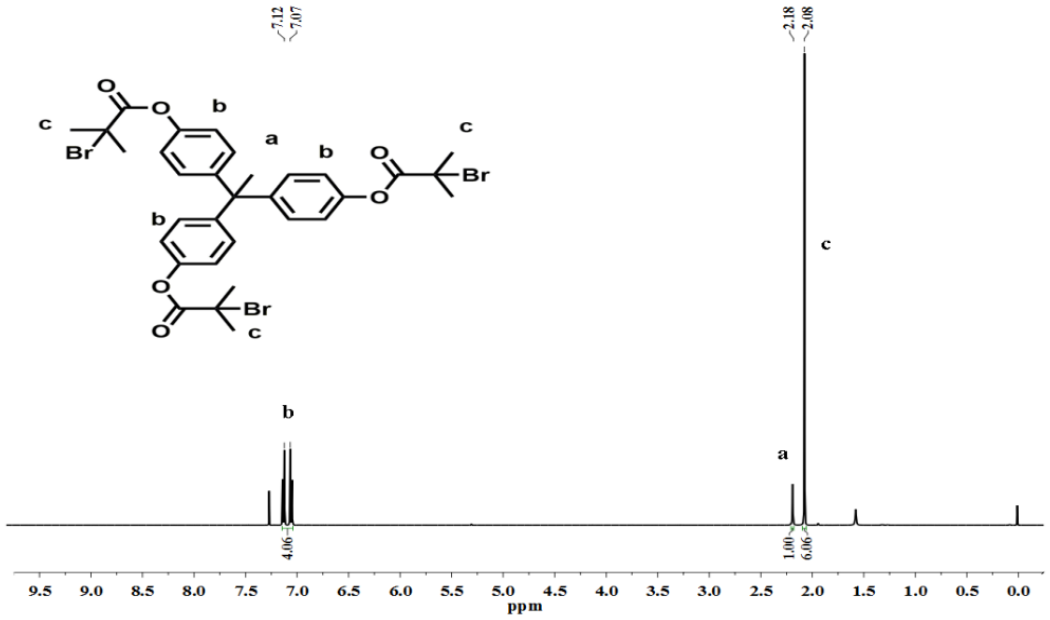
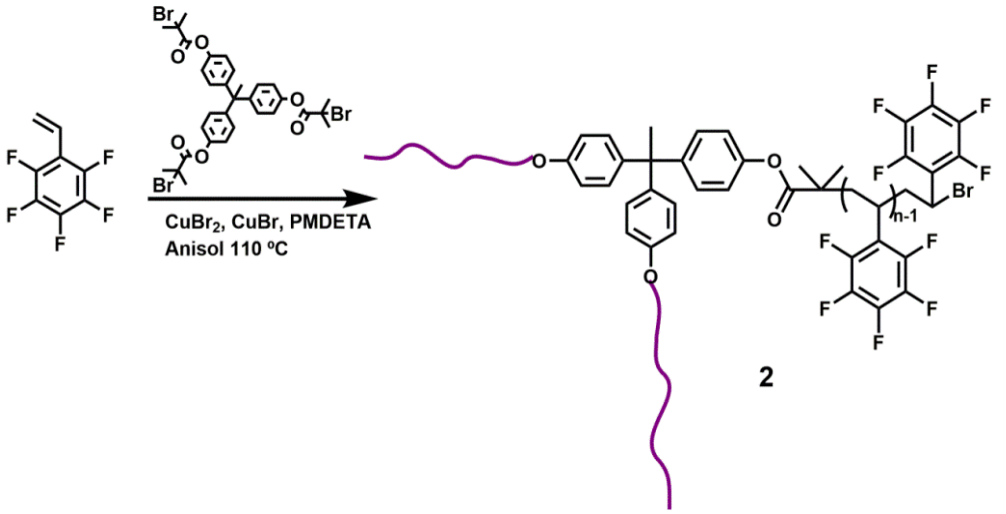


Figure 4.1: ^{1}H NMR spectrum of tris initiator (1) in $CDC1_3$.

4.2. Synthesis and Functionalization of 3-arm star polymer

4.2.1. Synthesis of polypentafluorostyrene 3-arm star polymer



(4.2)

In this study, after the preparation of the tris initiator, star polymer was produced. For this purpose Anisol, PMDETA, and CuBr, $CuBr_2$ were used in ATRP condition at 110ºC to give polypentaflurostyrene 3-arm star polymer and synthesized using the "core first" methodology Equation 4.2.

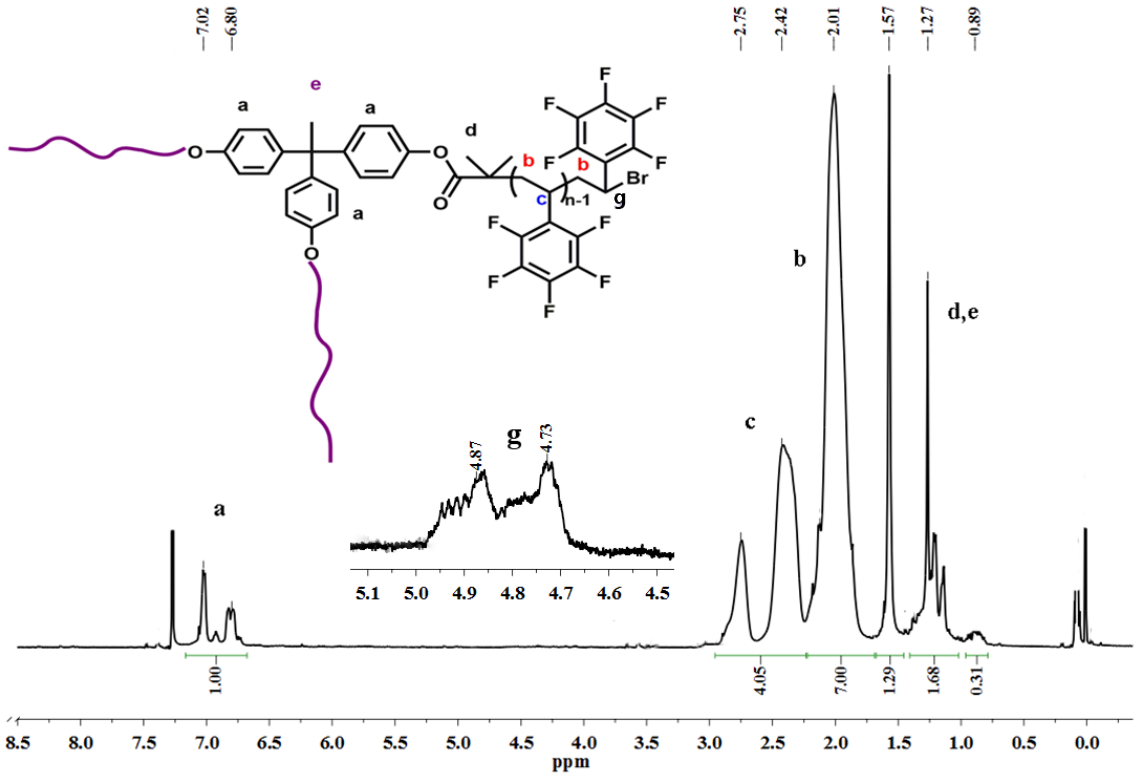


Figure 4.2: ^{1}H NMR spectrum of PPFS (2).

The ^{1}H NMR spectrum of 2 (Figure 4.2) showed that the Mn,NMR= 9293.76 g/mol of PPFS was determined from a ratio of integrated peaks at 7.27-6.79 ppm phenyl protons to sum of CH at 2.41ppm CH_2 at 2.01ppm next to pentaflurostyrene unit, so we found that sum of the repeating unit of PFS is 44.

$M_{n,NMR}$= 44X 194.1+753.36 (M_W of 2) = 9293,76 g/ mol

The ^{19}F NMR spectrum of **2** (Figure 4.3)showed meta fluorine at - 161.10 ppm, para fluorine at -154.23 ppm, orto fluorine at -143.30 ppm.

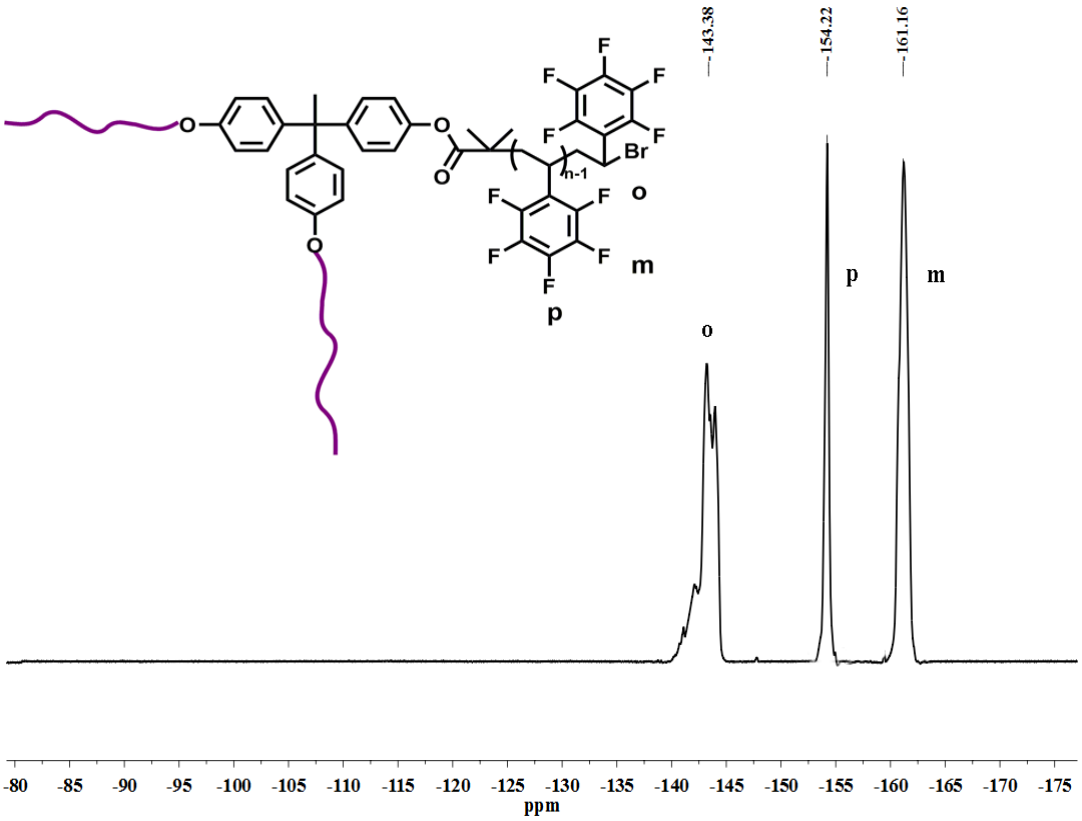


Figure 4.3: ^{19}F NMR spectrum of 2.

4.2.2. Thiol/para- fluorine ‘‘click’’ reaction with 1-octanethiol of PPFS star polymer

In the first experiment, 3-arm star polypentaflurostyrene reacted with 1.25 equiv of 1-octanethiol and 3 equiv Et_3N in DMF at 50 ^{o}C overnight. However, thiol/para click reaction did not occur at low temperature and low equivalent of reactants. ^{1}H NMR and ^{19}F NMR analyses show that 1-octanethiol did not click. From the ^{1}H NMR spectrum (Figure 4.4), the peaks of octanethiol especially CH_2S at 2.97 ppm were not detected. In addition, 1-octanethiol protons did not assingned in ^{1}HNMR analysis.

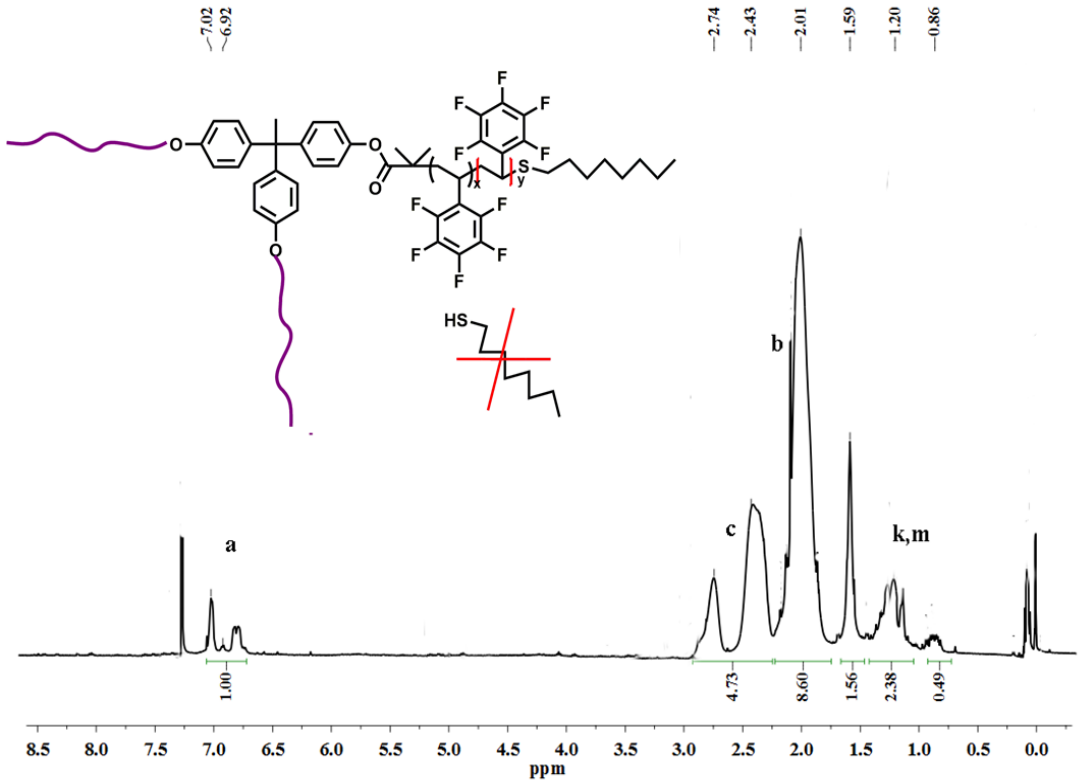


Figure 4.4: ^{1}H NMR spectrum of unproductive thiol/para fluorine click reaction of PPFS with 1-octanethiol.

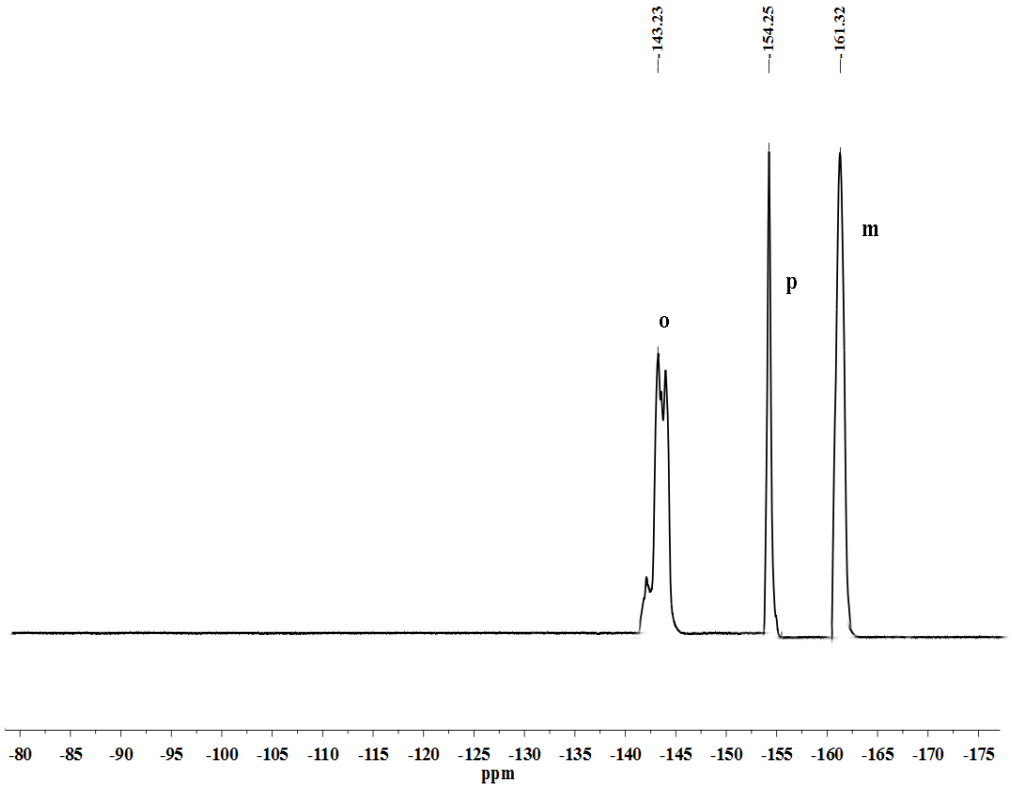
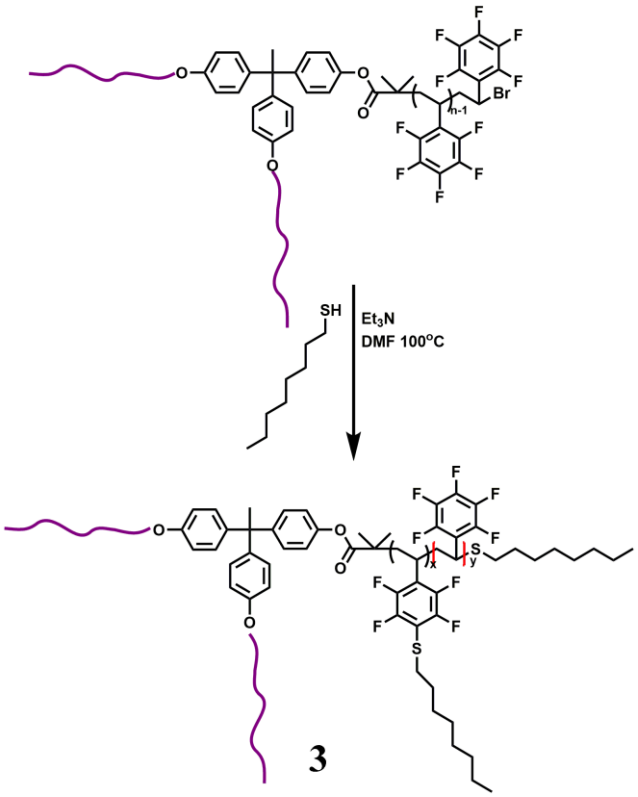


Figure 4.5: ^{19}F NMR spectrum of inefficient thiol/para fluorine click reaction of PPFS with 1-octanethiol.

From the ^{19}F NMR spectrum (Figure 4.5), there is no difference where ortho-meta and especially para fluorine, so F NMR showed that 1-octanethiol did not click to PPFS in this reaction condition.

When we improve the conditions, using the thiol/ para click reaction, polypentafluorostyrene 3-arm star polymer was reacted with 15 equiv of 1-octanethiol together with 15 equiv Et_3N as the base in DMF at 100 ^oC overnight as shown in Equation 4.3.



(4.3)

The H NMR spectrum Figure 4.6 showed CH_2S at 2.97 ppm and CH_2C*H*-PFS at 1.88 and 2.09-2.24 respectively. However, thiol/para fluorine click reaction did not occur efficiently 100%. 1-octantiol clicked six unit of PFS unit totally (x=6). Thirty-eight PFS unit did not react with octanthiol (y=38).

$\boldsymbol{M_{n,NMR}}$=(38x194.1)+(6x312)+819.65=10068g/mol

From ^{19}F NMR spectrum of the polymer Figure 4.7, the appearance of new signals correspond to orto fluorine of the product at -134.36 ppm and meta fluorine of **3** and ortho fluorine of **2** at -142.52 ppm. The spectrum show that para and meta fluorine of PPFS were at -108.69 and -99.01. As a result, 1-octanethiol did not click efficiently at 100%.

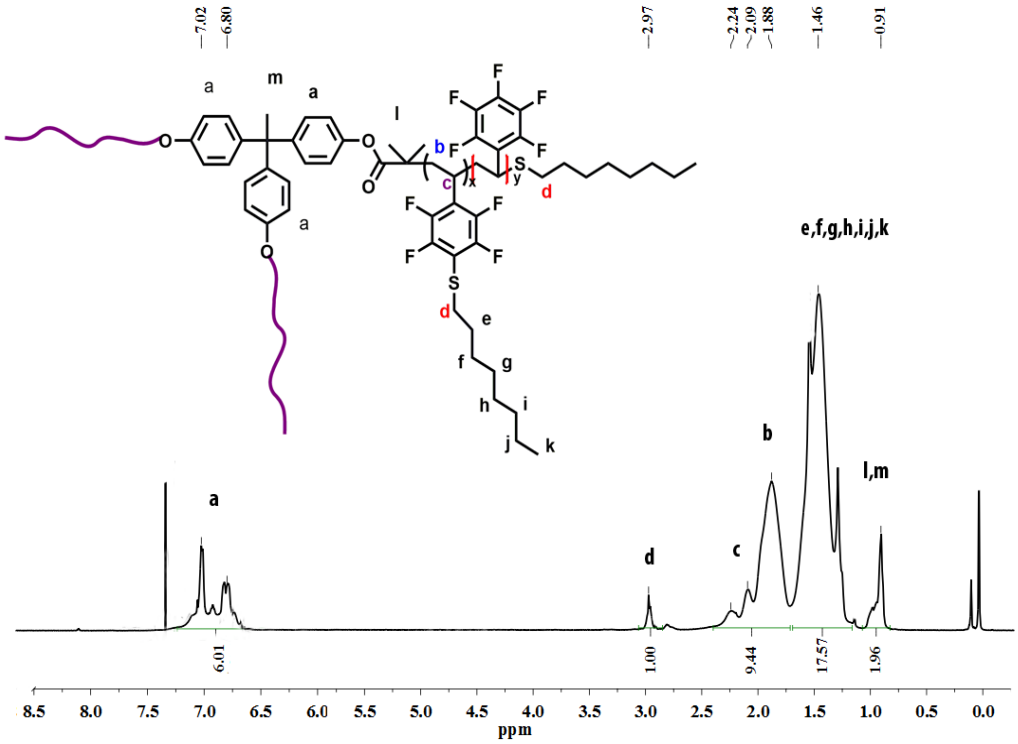


Figure 4.6: ^{1}H NMR spectrum of 3.

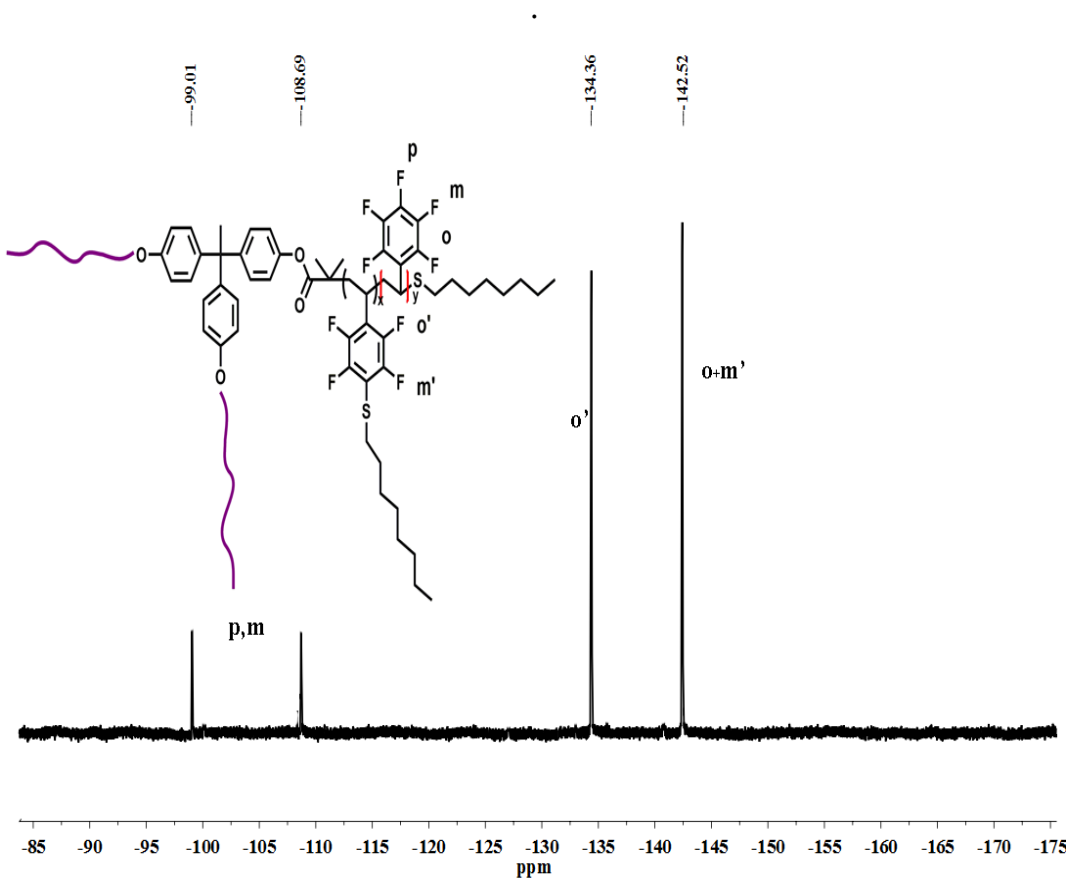


Figure 4.7: ^{19}F NMR spectrum of 3.

Table 4.1: The result of 3-arm star PPFS and thiol functionalized PPFS

	***PPFS*[a]**	***Thiol functionalized PPFS*[b]**
$M_{n,\,Theo}$**(g/mol)**	9033.6[c]	11937[d]
$M_{n,\,NMR}$**(g/mol)**	9293	10068
$M_{n,GPC}$ ***(g/mol)***	7888	8163
$M_{w,GPC}$ ***(g/mol)***	8414	8657
M_w/M_n ***(GPC)***	1.067	1.060
$M_{w,\,TD\text{-}GPC}$ **(g/mol)**	8898	9019
$M_{n,\,TD\text{-}GPC}$ ***(g/mol)***	8496	8593
$M_{p,\,TD\text{-}GPC}$ ***(g/mol)***	8421	8613
M_w/M_n ***(TD-GPC)***	1.047	1.05

[a] Synthesized by ATRP of Pentafluorostyrene in anisole using tris initiator, CuBr and $CuBr_2$ as a catalyst at 110 °C. $[M]_0:[I]_0 = 600$.
[b]Thiol/para fluro click reaction between PPFS and 1-octanethiol in DMF at 100 ^oC for overnight.
[c] $M_{n,\,Theo} = ([M]_o/[I]_o)$ X conversion % X M_W of monomer + M_W of initiator.
[d] $M_{n,\,Theo=}$ $M_{n\,,Theo}$ of PPFS+ M_w of initiotor(oktantiol-Br).

A monomodal GPC trace and narrow molecular weight distribution for 3-arm star polymers were detected as shown in Figure 4.8 Additionally, the molecular weight values (M_n, M_w, and M_p) of PPFS and thiol functionalized PPFS 3-armstar polymer obtained using conventional GPC and TD-GPC instruments was given in Table 4.1. It should be noted that there is a discrepancy between the molecular weight values obtained by conventional GPC and TD-GPC. This is expected because star polymers have more compact structures than linear polymer of equivalent molecular weight and composition that result in smaller hydrodynamic volume. Thus, apparent molecular weight of star polymers is underestimated by conventional GPC.

GPC analysis showed monomodal traces for the mentioned example. A clear shift was shown for GPC traces of these polymers. Furthermore, the GPC trace of thiol functionalized PS-*co*-PPFS displayed a shift to higher molecular weight region. From GPC measurement, $M_{n,GPC\ PPFS}$= 7888 g/mol and M_w/M_n= 1.067 were determined relative to PS standards in THF. $M_{n,GPC\ thiol\ functioaalized\ PPFS}$=8163 and M_w/M_n= 1.060.

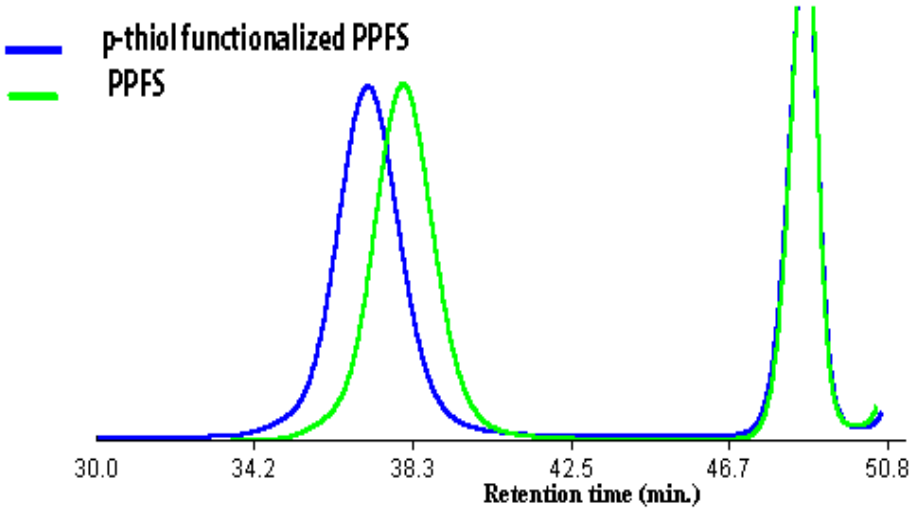


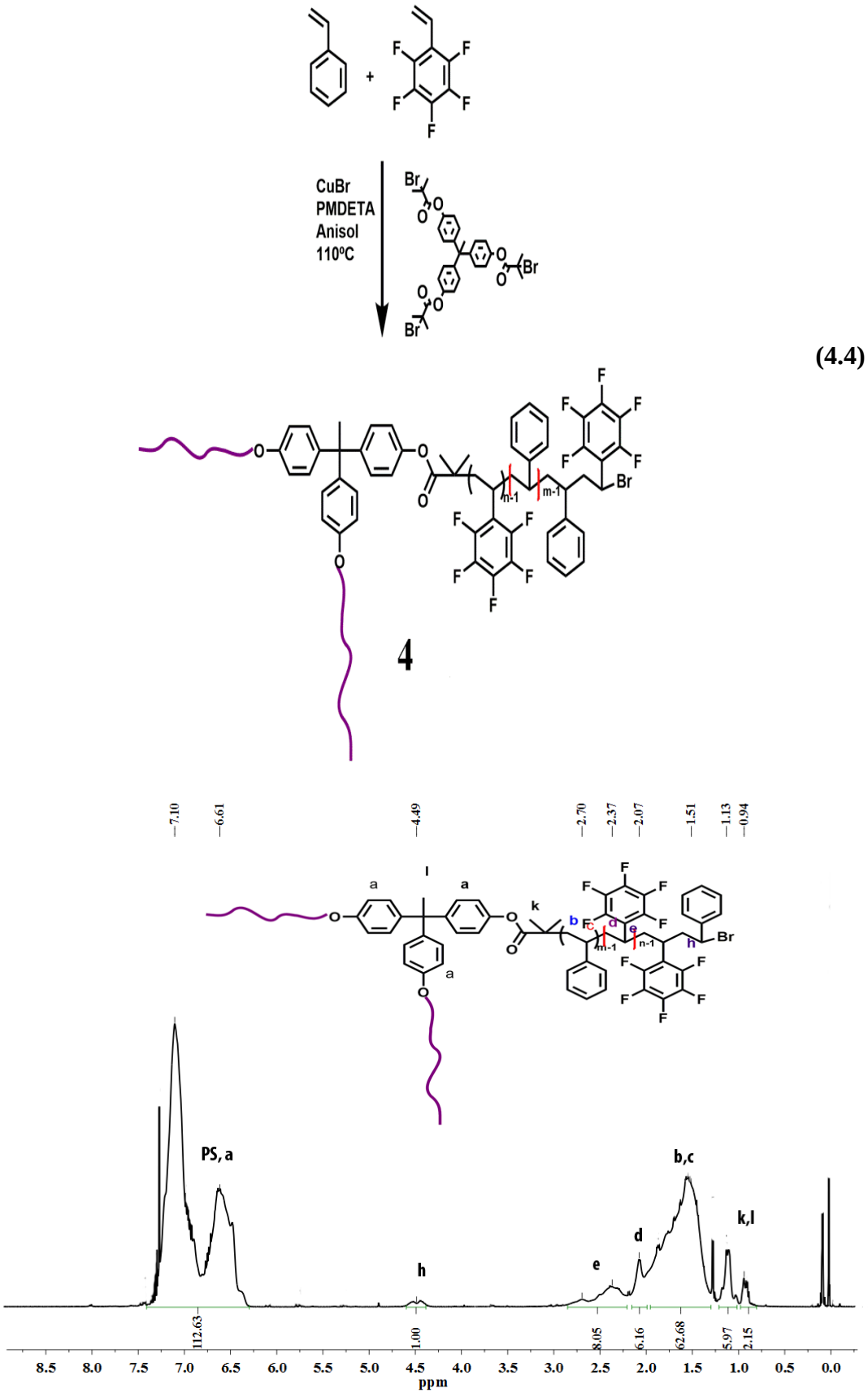
Figure 4.8: GPC traces of PPFS 3-arm star polymer and thiol functionalized PPFS 3-arm star polymer. GPC conditions: RI detector, relative to PS standards.

4.2.3. Synthesis of PS-*co*- PPFS 3-arm star polymer

After the preparation of the tris initiator, 3-arm star co-polymer was produced. For this purpose Anisol, PMDETA, and CuBr, were used in ATRP condition at 110 ºC to give polystyrene-*co*-polypentaflurostyrene 3-arm star polymer and this star polymer synthesized using the "core first" methodology Equation 4.2.

From ^{1}HNMR spectrum of PS-*co*-PPFS, phenyl protons were detected at 7.10-6.61 ppm, the peak of C*H*(St)Br at 4.49. CH_2 and C*H* of PFS in the repeating unit were at 2.07, 2.37-2.70 ppm respectivelyas shown in Figure 4.9. The peaks of CH_2 and C*H* of PS at 1.51 ppm were assigned. The initiator peaks were at 1.13-0.94. As a result, an integrated ratio of the C*H*.Br to the aryl protons of PS also gave the repeating unit of PS totally. (m=65). Also, an integrated ratio of the C*H*.Br to the CH_2 C*H* of PFS gave the repeating unit of PPFS (n=14). The 3-arm star copolymer consisted of $(PS)_{65}$-co-$(PPFS)_{14.}$

Mn_{NMR}= (65x104.15)+(14x194.1)+753.36 Mn_{NMR}= 10240 g/mol



(4.4)

Figure 4.9: ^{1}H NMR spectrum of $(PS)_{65}$-*co*-$(PPFS)_{14}$.

The ^{19}F NMR spectrum of **4** showed meta fluorine at -163.09 ppm, para fluorine at -158.45 ppm, and ortho fluorine at -141.60 ppm as shown in Figure 4.10.

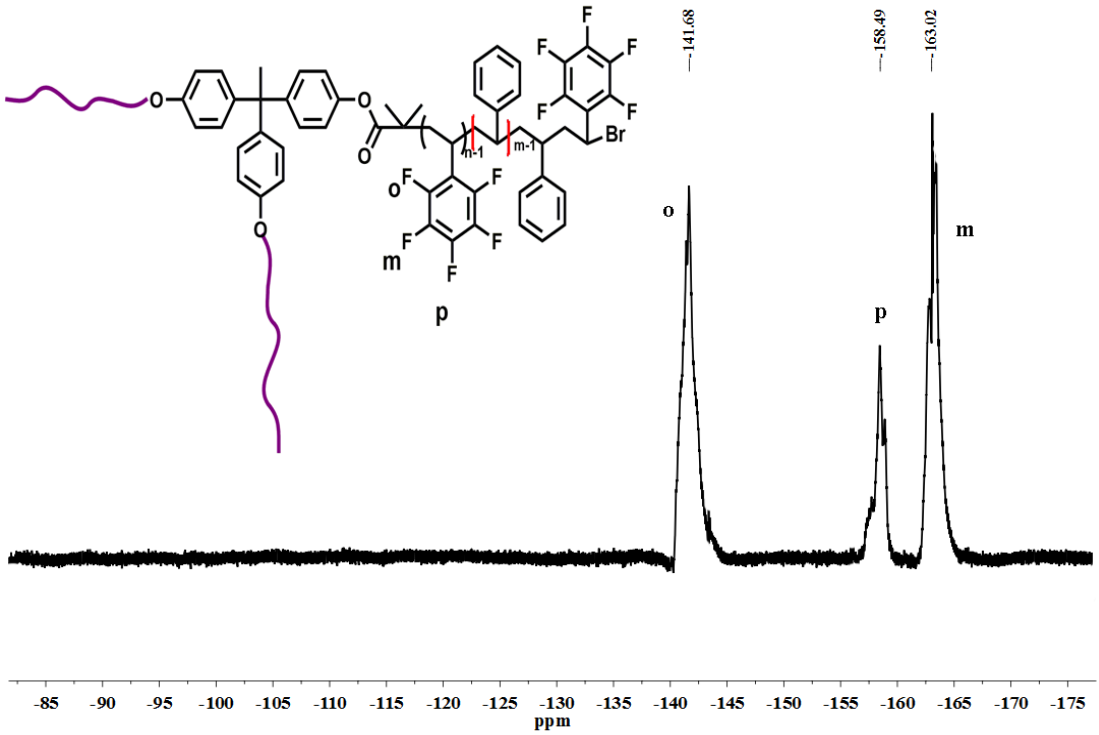


Figure 4.10: ^{19}F NMR spectrum of PS-*co*-PPFS 3-arm star polymer in $CDCl_3$.

4.2.4. Thiol/para- fluorine ‘‘click’’ reaction with 1-octanethiol of $(PS)_{65}$-*co*-$(PPFS)_{14}$ star polymer

In the first experiment, 3-arm star PS-*co*-PPFS reacted with 1.25 equiv of 1-octanethiol and 3 equiv Et_3N in DMF at 50 ^oC overnight.

From the ^1H NMR spectrum Figure 4.11, the peaks of octanethiol especially CH_2S at 2.82 ppm was not detected. As a result, thiol/para click reaction did not occur at low temperatures and low equivalent of reactants.

From the ^{19}F NMR spectrum Figure 4.12, there is no difference in ortho-meta and especially para fluorine, so ^{19}F NMR showed that 1-octanethiol did not click to $(PS)_{65}$-*co*-$(PPFS)_{14}$ in this reaction conditions.

In the second experiment using the thiol/ para click reaction, polystyrene-*co*-polypentafluorostyrene 3-arm star polymer was reacted with 15 equiv of 1-octanethiol together with Et_3N as a base in DMF at 100 ^oC overnight as shown in Equation 4.5.

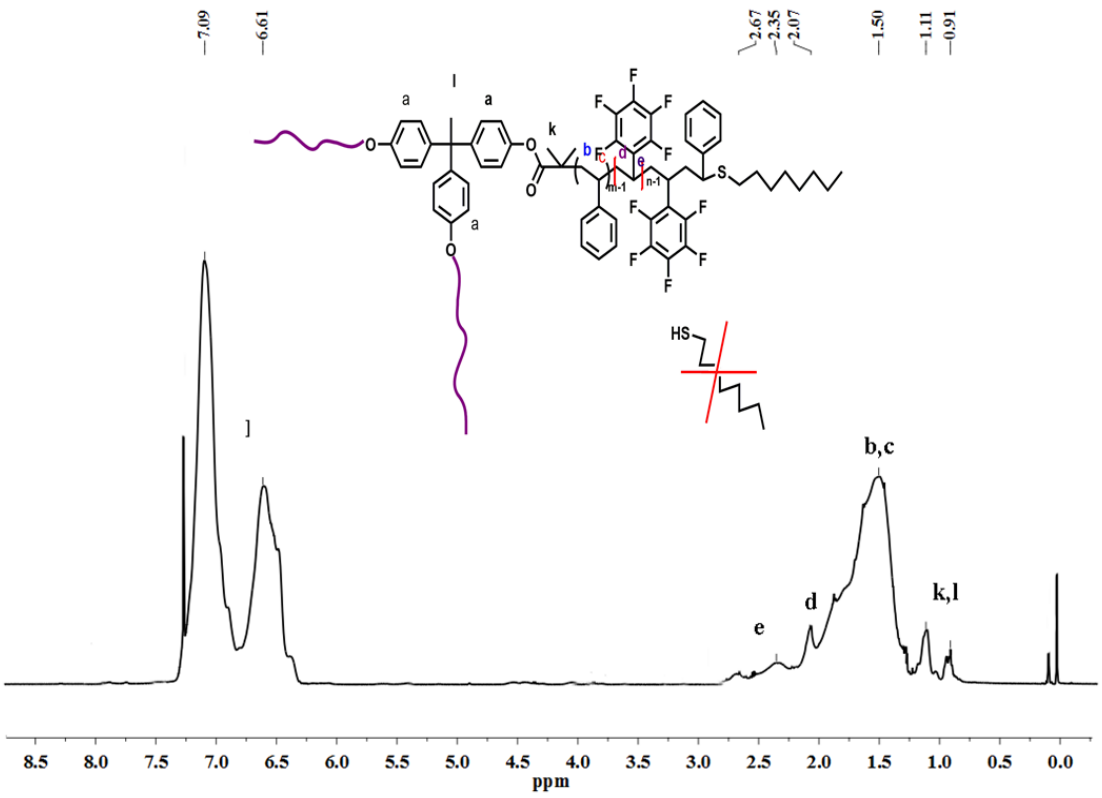


Figure 4.11: ^{1}H NMR spectrum of unproductive thiol/para fluorine click reaction of PS-*co*-PPFS with 1-octanethiol.

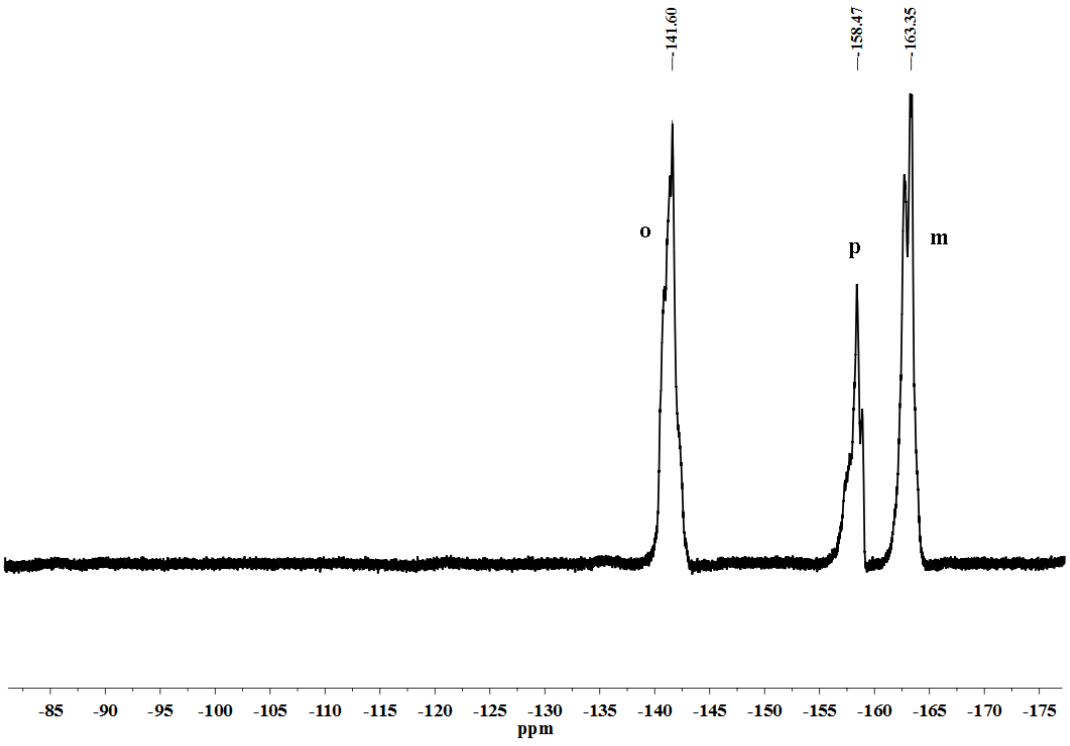
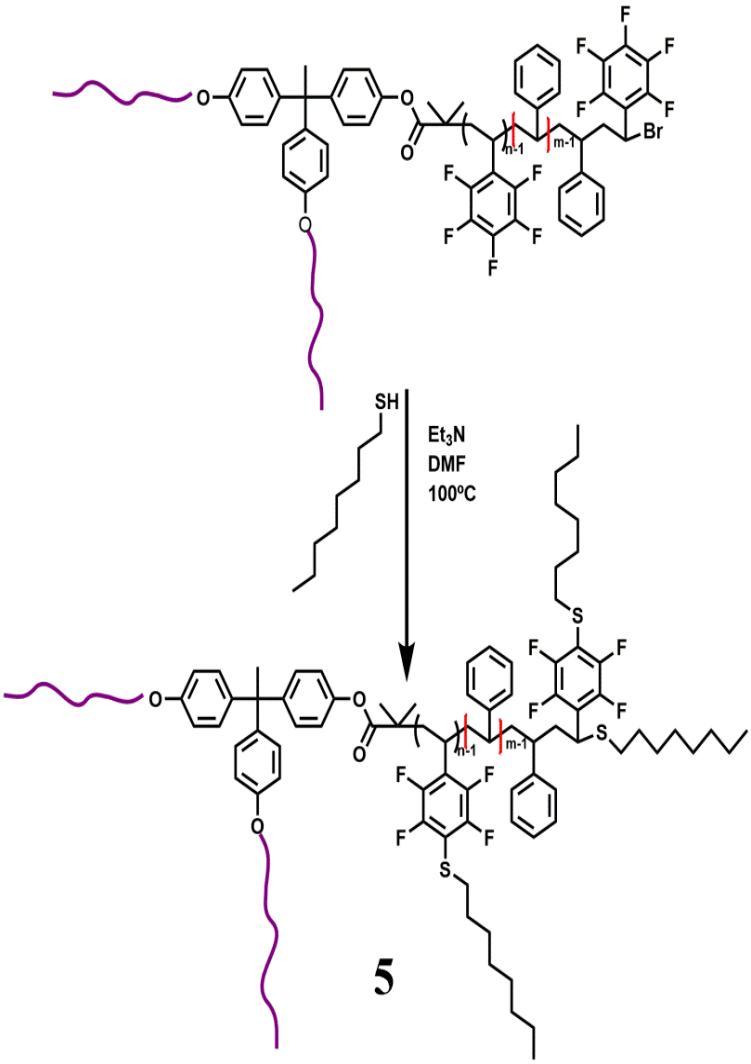


Figure 4.12: ^{19}F NMR spectrum of unproductive thiol/para fluorine click reaction of PS-*co*-PPFS with 1-octanethiol.



(4.5)

From the ^{1}H NMR spectrum as shown in Figure 4.13, it can be detected that the signals at 2.82 ppm are assignable to CH_2S of the 1-octanethiol. CH_2C*H*-PPFS signals were at 2.40 and 2.07 ppm respectively. However, CH_2C*H*-PS signals revealed at 1.56 ppm. The aryl protons of PS were at 6.59-7.06 ppm, and the signal -(CH_2)$_6$CH_3 of octanethiol protons at 1.31-1.44 ppm. The initiator protons were at 0.91 ppm.

An integrated area of aryl protons to CH_2S of 1-octanethiol gave that thiol/para click reaction occurred efficiently. Fourteen units of PPFS clicked with octanethiol completely.

From ^{19}F NMR spectrum of the polymer as shown in Figure 4.14 , the appearance of new signals corresponded to meta fluorine of the product at -141.44 ppm and ortho fluorine at -135.42 ppm. The signal of para fluorine of PS-*co*-PPFS disappeared.

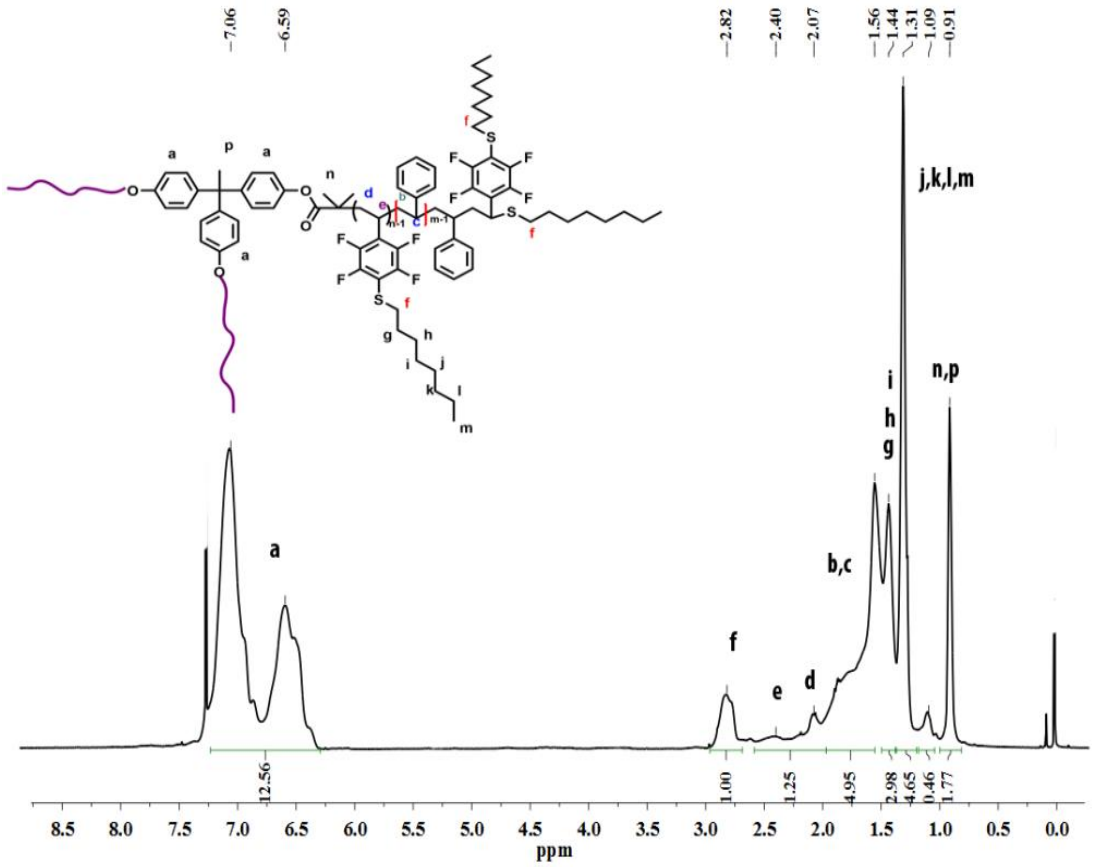


Figure 4.13: ^{1}H NMR spectrum of 5

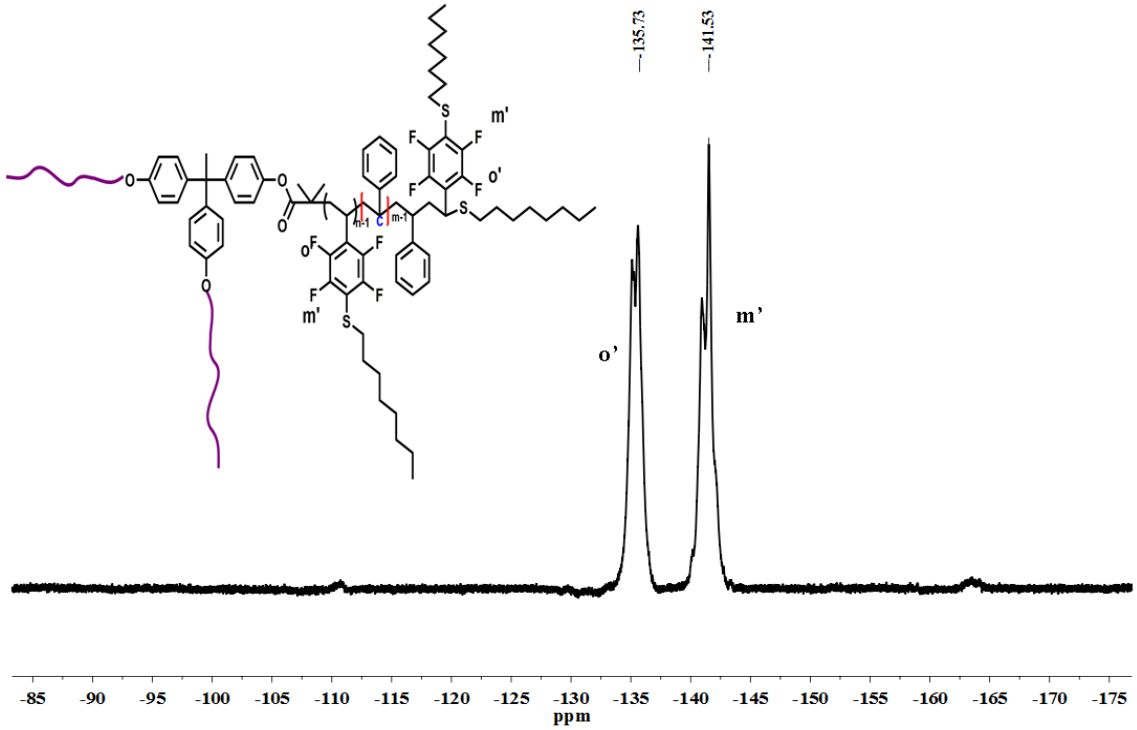


Figure 4.14: ^{19}F NMR spectrum of 5

Table 4.2: The result of 3-arm star PS-*co*-PFS and thiol functionalized PS-*co*-PPFS

	***PS-co-PPFS*[a]**	***Thiol functionalized PS-co-PPFS*[b]**
$M_{n,Theo}$ **(g/mol)**	10391[c]	11315[d]
$M_{n,NMR}$ **(g/mol)**	10240	12100
$M_{n,GPC}$ **(g/mol)**	11327	12035
$M_{w,GPC}$ **(g/mol)**	12120	14032
M_w/M_n **(GPC)**	1.070	1.16
$M_{w,TD\text{-}GPC}$ **(g/mol)**	11931	16187
$M_{n,TD\text{-}GPC}$ **(g/mol)**	11082	13885
$M_{p,TD\text{-}GPC}$ **(g/mol)**	10848	12636
M_w/M_n **(TD-GPC)**	1.077	1.166

[a] Synthesized by ATRP of styrene and pentaflurostyrene in anisole using CuBr as a catalyst and tris initiator , PMDETA at 110 °C. $[M]_0:[I]_0 = 600$ [M]styrene:[M]pentafluorostyrene = 10

[b]Thiol/ para fluoro click reaction between 1-octanethiol and PS-*co*-PPFS in DMF at 100°C for overnight.

[c] $M_{n,theo} = ([M]_o/[I]_o)$ X conversion % X [M_W of monomerstyrene+ (M_W of monomerpentaflurostyrene X [M]styrene/[M]pentaflurostyrene) + M_W of initiator.

[d] $M_{n,theo}$ = Mn_{Theo} of PS-*co*-PPFS+ M_W of initiator(oktantiol-Br)

A monomodal GPC trace and narrow molecular weight distribution for 3-arm star polymers were detected. Additionally, the molecular weight values (M_n, M_w, and M_p) of PPFS and thiol functionated PS-*co*-PPFS 3-armstar polymer obtained using conventional GPC and TD-GPC instruments were given in Table 4.2.

GPC analysis showed monomodal traces for the mentioned example. A clear shift was not shown for GPC traces of these polymers because of the hydrodynamic volume. Although the thiol/para click reaction of **4** occured, the GPC trace of **5** displayed a shift low molecular weight region because hydrodynamic volume was decreased.

$M_{n,GPC\ of\ 4}$ = 11327 g/mol M_w/M_n= 1.070 and $M_{n,\ GPC\ of\ 5}$ =12035 g/mol M_w/M_n=1.16

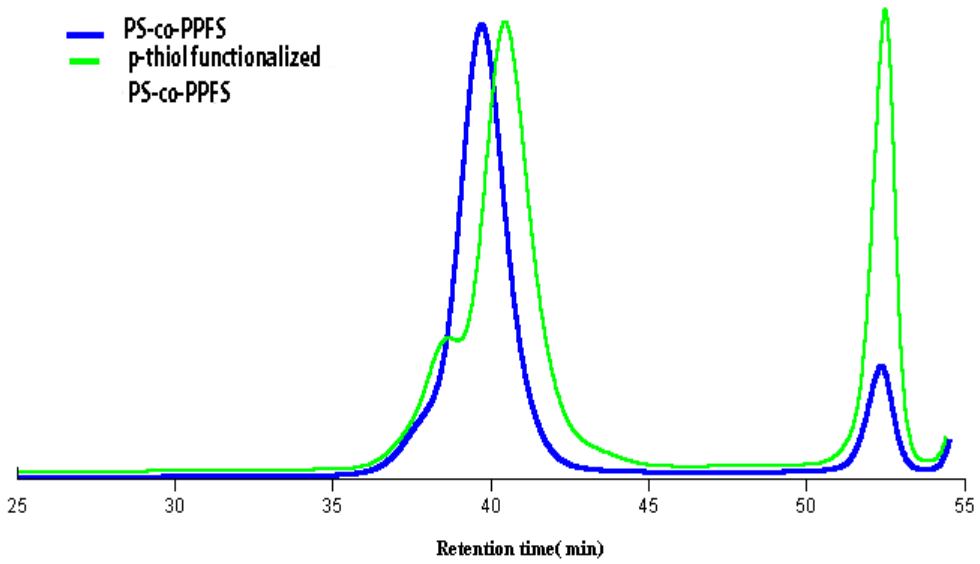


Figure 4.15: GPC trace of PS-*co*-PPFS 3-arm star polymer and thiol functionalized PS-*co*-PPFS 3-arm star polymer. GPC conditions: RI detector, relative to PS standards.

5. CONCLUSION

The aim of this M.Sc. thesis is to synthesize and modify well-defined 3-arm star homo and copolymers successfully by a combination of ATRP and thiol/para fluro click reactions.

In the first study, polypentaflurostyrene(PPFS) 3-arm star polymer was synthesized. For this purpose, first, we have prepared the tris initiator. It was synthesized by reaction of 1, 1, 1- tris (4- hydoxy-phenyl)ethane and 2-bromoisobutryl bromide. 3-arm star PPFS was obtained by using core-first method in ATRP. From ^{1}H NMR analysis we found the PFS repeating unit in the polymer. Then, 1-octanethiol was added to PPFS via thiol/para fluorine click reaction. Thiol/para fluro click reaction was proved by ^{19}F NMR. Moreover, GPC, TD-GPC and ^{1}H NMR analyses confirmed these polymers.

In the second study, polystyrene-*co*-pentaflurostyrene (PS-*co*-PPFS) 3-arm star polymer was synthesized. For this purpose, we prepared tris initiator. PS-*co*-PPFS 3-arm star polymer was obtained by using core-first strategy in ATRP. From ^{1}H NMR analysis we found the PPFS and PS repeating units in the polymer. The functionalization of (PS-*co*-PPFS) is obtained by thiol/para fluorine click reaction with 1-octanethiol. The click reaction of (PS-*co*-PPFS) was more efficient than the thiol/para fluro click reaction of PPFS. ^{19}F NMR, GPC, TD-GPC and ^{1}H NMR analysis confirmed these polymers.

In the future we will focus on the functionalization of 3-arm star PPFS and PS-*co*-PPFS polymer with a grand molecule structure as polyethylene glycol.

REFERENCES

[1] **S. Ebnesajjad , P.R. Khaladkar** «Fluoropolymer applications in chemical processing industries,» *Norwich, NY: William Andrew, Inc.; ,* 2005..

[2] **N. M. Hansen, K. Jankova and S. Hvilsted,** "Fluoropolymer materials and architectures prepared by controlled radical polymerizations," *European Polymer Journal,***43**, p. 255–293, (2007).

[3] **G. D. Fu, . E. T. Kang , . K. G. Neoh, C. C. Lin and D. J. Liaw,** "Rigid Fluorinated Polyimides with Well-Defined Polystyrene/ Poly(pentafluorostyrene) Side Chains from Atom Transfer Radical Polymerization," *Macromolecules,***38**, pp. 7593-7600, 2005.

[4] **G. D. Fu, S. J. Phua, . E. T. Kang and K. G. Neoh ,** "Tadpole-Shaped Amphiphilic Block-Graft Copolymers Prepared via Consecutive Atom Transfer Radical Polymerizations," *Macromolecules,***38**, pp. 2612-2619, 2005.

[5] **H. Kolb, M. Finn and K. Sharpless,** "Click chemistry: Diverse chemical function from a few good reactions," *Angewandte Chemie-International Edition,* **40**, pp. 2004-2021, 2001.

[6] **M. PAZ-PAZOS and C. PUGH,** "Synthesis, Isolation, and Thermal Behavior of Polybutadiene Grafted with Poly(2,3,4,5,6-pentafluorostyrene)," *Journal of Polymer Science: Part A: Polymer Chemistry,* **43**, p. 2874–2891, 2005.

[7] **K. Matyjaszewski,** «Controlled/living radical polymerizations: from synthesis to materials,» *ACS, Washington, DC: Oxford University Press,* 2006.

[8] **G. Odian,** " Principle of Polymerization," *John Wiley & Sons, New Jersey,* 2004.

[9] **M. Szwarc,** «Block copolymers,» *Nature,***178**, p. 1168, 1956.

[10] **R. P. Quirk, D. J. Kinning, L. J. Fetters ve S. L. Aggarwal,** «Comprehensive Polymer Science, » *Ed. Pergamon Press, London,***7**, p. 1, 1989.

[11] **S. Coca, H. Paik ve K. Matyjaszewski,** «Block Coplymers by Transformation of Living Ring-Opening Metathesis Polymerization into Controlled/“Living” Atom Transfer Radical Polymerization,» , **30**, pp. 6513-6516, 1997.

[12] **R. Quirk and B. Lee,** "Terminology and classification of quasiliving polymerizations and ideal living polymerizations on the basis of the logic of elementary polymerization reactions, and comments on using the term controlled," *4. Polym. Int,* **27**, p. 359, 1992.

[13] **K. Matyjaszewski and C. H. Lin,** "Naming of controlled living polymerizations," *Makromol. Chem. Macromolecules Symp.,* **47**, p. 221, 1991.

[14] **G. Litvinienko and A. H. E. Müler,** " General kinetic analysis and comparison of molecular weight distributions for various mechanisms of activity exchange in living polymerizations," *Macromolecules,* **30**, p. 1253, 1997.

[15] **J. Wang and K. Matyjaszewski,** "Controlled living radical polymerization -

atom-transfer radical polymerization in the presence of transition-metal complexes," *Journal of the American Chemical Society,***117**, pp. 5614-5615, 1995.

[16] **M. Kato, M. Kamigaito , M. Sawamoto and T. Higashimura,** "Polymerization of methyl-methacrylate with the carbon-tetrachloride dichlorotris (triphenylphosphine) ruthenium(ii) methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system - possibility of living radical polymerization," *Macromolecules,***28**, pp. 1721-1723, 1995.

[17] **M. Georges , R. Veregin , P. Kazmaier and G. Hamer,** "Narrow molecular-weight resins by a free-radical polymerization process," *Macromolecules,***26**, pp. 2987-2988, 1993.

[18] **J. Chiefari, Y. Chong, F. Ercole, J. Krstina, J. Jeffery, . T. Le, R. Mayadunne, G. Meijs, C. Moad, G. Moad, E. Rizzardo and S. Thang,** "Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process," *Macromolecules,* **31**, pp. 5559-5562, 1998.

[19] **T. Grimaud and K. Matyjaszewski,** "Controlled/"Living" radical polymerization of methyl methacrylate by atom transfer radical polymerization," *Macromolecules,***30**, p. 2216, 1997.

[20] **K. Matyjaszewski and J. Xia,** "Atom Transfer Radical Polymerization," *Chem. Rev*, **101**, pp. 2921-2990, 2001.

[21] **A. Goto and T. Fukuda,** "Determination of the Activation Rate Constants of Alkyl Halide Initiators for Atom Transfer Radical Polymerization," *Macromol. Rapid Commun.,***20**, pp. 633-636, 1999.

[22] **K. Matyjaszewski,** "Mechanistic and Synthetic Aspects of Atom Transfer Radical Polymerization," *Journal of Macromolecular Science-Pure and Applied Chemistry*, A**34**, pp. 1785-1801, 1997.

[23] **K. Matyjaszewski,** "Environmental aspects of controlled radical polymerization," *Macromol. Symp.,***152**, pp. 29-42, 2000.

[24] **U. Tunca , G. Hizal , M. Acar, M. Tasdelen, Y. Yagci and M. Mishra,** "Controlled/Living Radical Polymerization, in Handbook of Vinyl Polymers," *CRC Press Taylor & Francis Group,: New York*, pp. 256-281, 2009.

[25] **D. Benoit , V. Chaplinski , R. Braslau and C. Hawke,** "Development of a Universal Alkoxyamine for "Living" Free Radical Polymerizations," *J. Am. Chem. Soc,***121**, pp. 3904-3920., 1999.

[26] **C. Hawker , G. Barclay and J. Dao,** "Radical Crossover in Nitroxide Mediated "Living" Free Radical Polymerizations," *J. Am. Chem. Soc.,***118**, pp. 11467-11471, 1996.

[27] **R. Veregin , M. Georges , P. Kazmaier ve G. Hamer,** «Free-Radical Polymerizations for Narrow Polydispersity Resins - Electron-Spin-Resonance Studies of the Kinetics and Mechanism,» *Macromolecules,* **26**, pp. 5316-5320, 1993.

[28] **R. Veregin , M. Georges , G. Hamer and P. Kazmaier,** "Mechanism of Living Free-Radical Polymerizations with Narrow Polydispersity - Electron-Spin-Resonance and Kinetic-Studies," *Macromolecules,* **28**, pp. 4391-4398, 1995.

[29] **W. Skene , J. Scaiano, N. Listigovers, P. Kazmaier ve M. Georges,** «Rate Constants for the Trapping of Various Carbon-Centered Radicals by Nitroxides:

Unimolecular Initiators for Living Free Radical Polymerization,» *Macromolecules,* **33**, pp. 5065-5072, 2000.

[30] **B. Woodworth , Z. Metzner and K. Matyjaszewski,** "Copper Triflate as a Catalyst in Atom Transfer Radical Polymerization of Styrene and Methyl Acrylate," *Macromolecules,* **31**, pp. 7999-8004, 1998.

[31] **K. Matyjaszewski, Y. Gnanou and L. Leibler,** "Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications.," *Weinheim, Wiley-VCH.,* 2007.

[32] **W. Kuran,** "Coordination Polymerization of Heterocyclic And Heterounsaturated Monomers," *Prog. Polym. Sci., **23(6)**,* pp. 919-992, 1998.

[33] **R. Lundberg, E. Cox, Frish, K. and Reegen, S.,** "Lactones, in Ring-Opening Polymerization 2:247," *Marcel Dekker, New York.,* 1969.

[34] **G. Schwach , J. Coudane , R. Engel and M. Vert,** "Ring Opening Polymerization of D,L-Lactide in the Presence of Zinc Metal and Zinc Lactate, Polym. Initiated by Aluminum Isopropoxide Trimer or Tetramer," *Macromolecules, Int. **46(3)**,* pp. 177-182, 1998.

[35] **M. Wakioka , K. Baek , T. Ando , M. Kamigaito and M. Sawamoto,** "Possibility of living radical polymerization of vinyl acetate catalyzed by iron(I) complex," *Macromolecules,* **35**, pp. 330-333, 2002.

[36] **H. Durmaz , A. Sanyal, G. Hizal and U. Tunca,** *Polym. Chem.,* **3,** pp. 825-835, 2012.

[37] **K. Matyjaszewski, T. Patten and J. Xia,** "Controlled/"living" radical polymerization. Kinetics of the homogeneous atom transfer radical polymerization of styrene," *Journal of the American Chemical Society,* **119**, pp. 674-680, 1997.

[38] **K. Matyjaszewski , K. Davis , T. Patten ve M. Wei,** «Observation and analysis of a slow termination process in the atom transfer radical polymerization of styrene, Tetrahedron,» **53**, pp. 15321- 15329, 1997.

[39] **I. Hamley,** «The Physics of block copolymers» *Oxford University Press, Oxford.,* 1998.

[40] **O. Diels, K. Alder and J. Liebigs,** *Ann. Chem,* **460**, p. 98–122, 1928.

[41] **T. Posner,** "Beiträge zur kenntniss der ungesättigten verbindungen. Ii. Ueber die addition von mercaptanen an ungesättigte kohlenwasserstoffe" *Berichte der deutschen chemischen Gesellschaft* , **38**, pp. 646-657, 1905.

[42] **F. Mayo and C. Walling,** "The peroxide effect in the addition of reagents to unsaturated compounds and in rearrangement reactions," *Chemical Reviews,* **27**, pp. 351-412, 1940.

[43] **K. Griesbaum,** «Problems and possibilities of the free-radical addition of thiols to unsaturated compounds,» *Angewandte Chemie International Edition in English **9**,* pp. 273-287, 1970.

[44] **J. Braun ve R. Murjahn,** «Haftfestigkeit organischer reste (iv)» *Berichte der deutschen chemischen Gesellschaft (A and B Series),* **59**, pp. 1202-1209, 1926.

[45] **W. Cook, F. Chen, D. Pattison , P. Hopson and M. Beaujon,** "Thermal polymerization of thiol-ene network-forming systems" *Polymer International,* **56**, pp. 1572-1579, 2007.

[46] **J. Carioscia , J. W. Stansbury and C. Bowman,** "Evaluation and control of

thiol-ene/thiol-epoxy hybrid networks.," *Polymer **48, (6)**,*, pp. 1526-1532, 2007.

[47] **A. Dondoni,** "The emergence of thiol–ene coupling as a click process for materials and bioorganic chemistry," *Angewandte Chemie International Edition **47***, pp. 8995-8997, 2008.

[48] **K. Kempe , A. Krieg, C. R. Becer and U. S. Schubert,** "‘‘Clicking’’ on/with polymers: a rapidly expanding field for the straightforward preparation of novel macromolecular architectures," *Chem. Soc. Rev,* **41**, p. 176–191, 2012.

[49] **J. W. Chan , B. Yu , C. E. Hoyle and A. Lowe,** "The nucleophilic, phosphine-catalyzed thiol-ene click reaction and convergent star synthesis with raft-prepared homopolymers," *Polymer **50, (14)**,*, pp. 3158-3168, 2009.

[50] **C. Becer , K. Kokado , C. Weber , A. Can , Y. Chujo and U. Schubert,** "Metal-free synthesis of responsive polymers: cloud point tuning by controlled ‘click’ reaction," *J Polym Sci Part A: Polym Chem **48(6)***, p. 1278–86, 2010.

[51] **S. Slavin, J. Burns, D. Haddleton and C. Becer,** "Synthesis of glycopolymers via click reactions," *European Polymer Journal **47***, p. 435–446, 2011.

[52] **R. Huisgen,** «1.3-Dipolare Cycloadditionen,» *Ruckschau Und Ausblick, Angew. Chem. Int. Ed., **75***, pp. 604-637, 1963.

[53] **C. Tornoe , C. Christensen and M. Meldal,** "Peptidotriazoles on Solid Phase: 1,2,3 -Triazoles by Regiospecific Copper(I)-Catalyzed 1,3-Dipolar Cycloadditions of Terminal Alkynes to Azides," *J. Org. Chem., **67***, pp. 3057-3064, 2002.

[54] **S. Kamijo , T. Jinb and Y. Yamamotoa ,** "Four-component coupling reactions of silylacetylenes, allyl carbonates, and trimethylsilyl azide catalyzed by a Pd(0)-Cu(I) bimetallic catalyst. Fully substituted triazole synthesis from seemingly internal alkyalkynes," *Tetrahedron Letters ,**45,** ,* pp. 689-691, 2004.

[55] **S. Hotha, R. Anegundi and A. Natu,** "Expedient synthesis of 1,2,3 triazole-fused tetracyclic compounds by intramolecular Huisgen (click) reactions on carbohydrate-derived azido-alkynes," *Tetrahedron Letters,**46**,* pp. 4585-4588., 2005.

[56] **H. Zhao, . E. S. Sterner, E. Coughlin and P. Theato,** "o-Nitrobenzyl Alcohol Derivatives: Opportunities in Polymer and Materials Science," *Macromolecules, **45 (4)**,* p. 1723–1736, 2012.

[57] **O. Diels and K. Alder,** "Synthesen in der hydroaromatischen Reihe,," *Justus Liebig's Annalen der Chemie, **460,*** pp. 98-122, 1928.

[58] **E. Corey,** "Catalytic enantioselective Diels-Alder reactions: Methods, mechanistic fundamentals, pathways, and applications," *Angewandte Chemie-International Edition, **41,*** pp. 1650-1667, 2002.

[59] **O. Diels and K. Alder,** "Über die Ursachen der Azoesterreaktion" *Justus Liebig's Annalen der Chemie, **450,*** pp. 237-254, 1926.

[60] **J. Ripoll, A. Rouessac and F. Rouessac,** *Tetrahedron, **34,*** p. 19–40., 1978.

[61] **F. Fringuelli and A. Taticchi,** "The Diels Alder reaction : selected practical methods" *Chichester, New York, Wiley.*, 2002.

[62] **M. Tasdelen,** *Polym. Chem.,**2,**,* p. 2133, 2011.

[63] **A. Dag , M. Aydin , H. Durmaz, G. Hizal ve U. Tunca,** *J. Polym. Sci. Part A: Polym. Chem., **50***, pp. 4476-4483, 2012.

[64] **V. Long, G. Berry and L. Hobbs,** "Solution and Bulk Properties of Branched

Polyvinyl acetates IV—Melt viscosity" *Polymer, **5*** pp. 517-524, 1964.

[65] **N. Hadjichristidis , H. Iatrou , M. Pitsikalis and J. Mays,** "Macromolecular architectures by living and controlled/living polymerizations" *Progress in Polymer Science, **31*** pp. 1068-1132, 2006.

[66] **N. Hadjichristidis,** "Synthesis of miktoarm star (mu-star) polymers" *Journal of Polymer Science Part a-Polymer Chemistry, **37***, pp. 857-871, 1999.

[67] **J. Kennedy and S. Jacob,** "Cationic polymerization astronomy. Synthesis of polymer stars by cationic means," *Accounts of Chemical Research, **31***, pp. 835-841, 1998.

[68] **H. Hsieh and R. Quirk,** "Star Polymers, in, Anionic Polymerization, Principles and Practical Applications," *Marcel Dekker, New York*, pp. 333-368, 1996.

[69] **Y. Gnanou and D. Taton,** "Stars and Dendrimer-Like Architectures by the Divergent Method Using Controlled Radical Polymerization," *Macromolecular Symposia, **174,*** pp. 333-341, 2001.

[70] **A. Blencowe , J. Tan, T. Goh and G. Qiao,** "Core cross-linked star polymers via controlled radical polymerisation" *Polymer, **50,*** pp. 5-32, 2009.

[71] **M. Morton , S. Gadkary and F. Bueche,** "Preparation and Properties of Monodisperse Branched Polystyrene," *J Polymer Science, **57***, pp. 471-482, 1962.

[72] **T. Orofino and W.F.,** "Dilute Solution Properties of Branched Polymers, Polystyrene Trifunctional Star Molecules" *J Phys Chem,**67***, pp. 566-575, 1963.

[73] **M. R.,** "Organized Structures in Amorphous Styrene/Cis- 1,4-Isoprene Block Copolymers: Low Angle X-Ray Scattering and Electron Microscopy" *Polymer, **15,*** pp. 137-145, 1974.

[74] **J. Roovers, L. Zhou , P. Toporowski , M. Vanderzwan , H. Iatrou and N. Hadjichristidis,** "Regular Star Polymers with 64 and 128 Arms - Models for Polymeric Micelles" *Macromolecules, **26,*** pp. 4324-4331, 1993.

[75] **L. Zhou and J. Roovers ,** "Synthesis of Novel Carbosilane Dendritic Macromolecules" *Macromolecules, **26***, pp. 963-968, 1993.

[76] **K. Babiuch, D. Pretzel, T. Tolstik, A. Vollrath, S. Stanca, F. Foertsch, R. Becer, M. Gottschaldt, C. Biskup and U. Schubert,** "Uptake of Well-Defined, Highly Glycosylated, Pentafluorostyrene-Based Polymers and Nanoparticles by Human Hepatocellular Carcinoma Cells, *Macromol. Biosci.,**12***, p. 1190–1199 , 2012.

[77] **K. Babiuch, D. Pretzel, T. Tolstik, A. Vollrath, S. Stanca, F. Foertsch, C. Becer, M. Gottschaldt, C. Biskup and U. Schubert** , "Functionalized, Biocompatible Coating for Superparamagnetic Nanoparticles by Controlled Polymerization of a Thioglycosidic Monomer" *Biomacromolecules,**12***, p. 681–691, 2011.

[78] **L. Lou, Y. Koike and Y. Okamoto,** "Synthesis and Properties of Copolymers of Methyl Methacrylate with 2,3,4,5,6-Pentafluoro and 4-Trifluoromethyl 2,3,5,6-Tetrafluoro Styrenes: An Intrachain Interaction between Methyl Ester and Fluoro Aromatic Moieties," *Journal of Polymer Science: Part A: Polymer Chemistry, Vol. **48,*** p. 4938–4942, 2010.

[79] **Y. Wan, X. Fei, Z. Shi, J. Hu, X. Zhan, L. Zhao, C. Chen, Z. Cui and D. Zhang,** "Highly Fluorinated Low-Molecular-Weight Photoresists for Optical Waveguides," *Journal of Polymer Science: Part A: Polymer Chemistry, Vol. **49***,

p. 762–769, 2011.

[80] **K. T. Powell, C. Cheng and K. L. Wooley,** "Complex Amphiphilic Hyperbranched Fluoropolymers by Atom Transfer Radical Self-Condensing Vinyl (Co)polymerization" *Macromolecules* , ***40,*** pp. 4509-4515, 2007.

[81] **I. Dimitrov, K. Jankova and S. Hvilsted,** "Controlled Synthesis of Fluorinated Copolymers with Pendant Sulfonates," *Journal of Polymer Science: Part A: Polymer Chemistry, Vol.* ***46,*** p. 7827–7834, 2008.

[82] **V. Atanasov and J. Kerres,** "Highly Phosphonated Polypentafluorostyrene" *Macromolecules* ,***44,*** p. 6416–6423, 2011.

[83] **A. Bonilla, A. Bousquet, E. Ibarboure, E. Papon, C. Labrugere and J. Rodrıguez-Hernandez,** "Fabrication and Superhydrophobic Behavior of Fluorinated Microspheres" *Langmuir* ,***26(22),*** p. 16775–16781, 2010.

[84] **J. Rodriguez-Hernandez, A. Munoz-Bonilla, A. Bousquet, E. Ibarboure and E. Papon,** "Environmentally Responsive Particles: From Superhydrophobic Particle Films to Water-Dispersible Microspheres" *Langmuir,* ***26(24)****,* p. 18617–18620, 2010.

CURRICULUM VITAE

Name Surname: Gizem PALAK

Place and date of birth: Üsküdar, 22/06/1989

E-Mail: **gzmpalak@yahoo.com**

B.Sc.: Istanbul University, Faculty of Engineering,
Chemistry Department , Istanbul-Avcılar.

M.Sc.: Istanbul Technical University
Faculty of Science and Letters,
Chemistry Department, Istanbul-Maslak